

=> file reg

FILE 'REGISTRY' ENTERED AT 10:15:49 ON 18 SEP 2002
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FILE 'REGISTRY' ENTERED AT 09:27:28 ON 18 SEP 2002
E 4-TERT-BUTYLCATECHOL/CN

L1 1 SEA 4-TERT-BUTYLCATECHOL/CN

FILE 'HCA' ENTERED AT 09:32:06 ON 18 SEP 2002

L2 2372 SEA L1 OR ?BUTYLCATECHOL?

L3 347615 SEA DISTILL? OR DIST# OR DISTN# OR CODISTILL? OR CODIST#
OR CODISTN# OR AZEOTROP? OR COAZEOTROP?

L4 242 SEA L2 AND L3

L5 992 SEA L1

L6 52 SEA L5 AND L3

FILE 'REGISTRY' ENTERED AT 09:32:56 ON 18 SEP 2002
E STYRENE/CN

L7 1 SEA STYRENE/CN

L8 3 SEA METHYLSTYRENE/CN

FILE 'HCA' ENTERED AT 09:37:39 ON 18 SEP 2002

L9 344960 SEA L7 OR L8 OR ?STYREN? OR ?STYRYL? OR VINYLAROM? OR
VINYL?(2A) (AROM# OR AROMATIC?)

L10 85 SEA L4 AND L9

L11 15 SEA L10 AND L5

L12 251293 SEA MONOMER?

L13 30 SEA L10 AND L12

L14 8 SEA L13 AND L5

FILE 'REGISTRY' ENTERED AT 09:41:37 ON 18 SEP 2002
E OXYGEN/CN

L15 1 SEA OXYGEN/CN

L16 1 SEA OXYGEN/CN

FILE 'LCA' ENTERED AT 09:44:12 ON 18 SEP 2002

L17 3529 SEA L16 OR AIR# OR OXYGENA? OR O2 OR (OXYGEN# OR
O) (2A) (ATM# OR ATMOS? OR GAS## OR GASIF? OR GASEOUS? OR
TREAT? OR PRETREAT? OR INTRODUC? OR INJECT? OR JET OR
JETS OR PORT OR PORTS OR PORTAL? OR NEEDL? OR SYRING? OR
APPLY? OR APPLIED OR APPLICATION?)

FILE 'HCA' ENTERED AT 09:49:33 ON 18 SEP 2002

L18 11 SEA L10 AND L17

L19 46190 SEA L7 OR L8

L20 33 SEA L10 AND L19
L21 12 SEA L20 AND L5
L22 22 SEA L11 OR L14 OR L18 OR L21
L23 34 SEA (L13 OR L20) NOT L22
L24 QUE NITRO# OR DINITRO# OR NO2 OR AMINO# OR DIAMINO# OR
NH2
L25 31 SEA L23 NOT L24
L26 14 SEA L22 NOT L24
L27 8 SEA L22 NOT L26
L28 3 SEA L23 NOT L25

FILE 'REGISTRY' ENTERED AT 10:15:49 ON 18 SEP 2002

=> file hca

FILE 'HCA' ENTERED AT 10:16:08 ON 18 SEP 2002

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=> d l26 1-14 cbib abs hitstr hitind

L26 ANSWER 1 OF 14 HCA COPYRIGHT 2002 ACS

135:5995 Composition and method for inhibiting polymerization and polymer growth. Benage, Brigitte; Abruscato, Gerald J.; Sikora, David J.; Grewal, Ruben S. (Uniroyal Chemical Company, Inc., USA). PCT Int. Appl. WO 2001040404 A1 20010607, 96 pp. DESIGNATED STATES: W: BR, CA, CN, ID, JP, KR, MX, SG; RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR. (English). CODEN: PIXXD2. APPLICATION: WO 2000-US31101 20001113. PRIORITY: US 1999-PV168623 19991203; US 2000-580343 20000525.

AB The method for inhibiting the premature polymn. and the polymer growth of ethylenically unsatd. **monomers** comprises adding an effective amt. of .gtoreq.1 hydrogen donor or electron acceptor inhibitor. Thus, 4-oxo-TEMPO 300 and diethylhydroxylamine 3000 ppm were mixed with **styrene**, showing only 20% increase in wt. of insol. polymer after 7 h, comparing 684% when only 4-oxo-TEMPO was used.

IT 98-29-3

(inhibiting polymn. and polymer growth)

RN 98-29-3 HCA

CN 1,2-Benzenediol, 4-(1,1-dimethylethyl)- (9CI) (CA INDEX NAME)

Bu-t

HO

OH

- IC ICM C09K015-04
ICS C07C007-20
CC 35-3 (Chemistry of Synthetic High Polymers)
IT **Distillation**
(for purifn. of **monomers**; inhibiting polymn. and polymer growth)
- IT 79-74-3 84-54-8, 2-Methylantraquinone 88-58-4 95-31-8,
N-tert-Butyl-2-benzothiazolesulfenamide 95-71-6 **98-29-3**
100-15-2 100-64-1 106-51-4, 2,5-Cyclohexadiene-1,4-dione, uses
130-15-4, 1,4-Naphthoquinone 530-17-6 536-74-3, Phenylacetylene
613-31-0, Dihydroanthracene 621-07-8, Dibenzylhydroxylamine
2154-35-0 2154-37-2 2154-69-0 2226-96-2 2406-25-9
2460-77-7 2516-88-3 2516-91-8 2516-92-9 2564-83-2
2564-88-7 3081-01-4 3225-24-9 3225-25-0 3229-53-6
3551-21-1 3710-84-7 3936-30-9 4130-42-1 6599-87-7
7078-98-0 7440-50-8, Copper, uses 14329-20-5 14691-88-4
21450-72-6 23037-14-1 24799-67-5 32154-44-2 34272-83-8
37149-18-1 38078-71-6 38632-29-0 38632-35-8 40289-91-6
54416-73-8 61015-94-9 71335-68-7 77432-44-1 87773-28-2
94271-84-8 103630-30-4 118191-03-0 123772-30-5 133406-90-3
153784-62-4 179552-47-7 179552-48-8 184160-78-9 188526-94-5
189291-86-9 342046-68-8 342046-71-3 342046-72-4 342046-73-5
342046-74-6 342046-75-7 342046-76-8 342046-77-9 342046-78-0
342046-79-1 342046-80-4 342046-81-5 342046-82-6 342046-83-7
342046-84-8 342046-85-9
(inhibiting polymn. and polymer growth)
- L26 ANSWER 2 OF 14 HCA COPYRIGHT 2002 ACS
132:208289 Polymerization inhibitor compositions for **vinyl aromatic monomers** such as **styrene** containing dihydroxyarenes and nitroxides. Shahid, Muslim (Baker Hughes Incorporated, USA). PCT Int. Appl. WO 2000014039 A1 20000316, 19 pp. DESIGNATED STATES: W: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK, ES, FI, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG. (English). CODEN: PIXXD2. APPLICATION: WO 1999-US20529 19990908. PRIORITY: US 1998-150488 19980909.
- AB The polymn. of **vinyl arom.** compds. such as **styrene** are inhibited by the addn. of a compn. that contains a dihydroxyarene or an alkyl-dihydroxyarene, a hydrogen transfer agent, a stable nitroxide, and optionally an org. amine. Thus, freshly **distd. styrene** was heated at 118.degree. for 90 min with an inhibitor compn. (2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl 125, Tetralin 103, and 2,5-di-tert-butylhydroquinone 174 ppm in n-octyl amine) giving 0.24% polymer compared with 36% without the inhibitor compn.
- IT **98-29-3**, 4-tert-Butylpyrocatechol

(vinyl arom. monomer polymn.
inhibitor compns. comprising dihydroxyarenes, nitroxides,
hydrogen transfer agent, and optionally org. amines)

RN 98-29-3 HCA
CN 1,2-Benzenediol, 4-(1,1-dimethylethyl)- (9CI) (CA INDEX NAME)

Bu-t

HO

OH

IT 100-42-5, Styrene, miscellaneous
25013-15-4, Vinyltoluene
(vinyl arom. monomer polymn.
inhibitor compns. comprising dihydroxyarenes, nitroxides,
hydrogen transfer agent, and optionally org. amines)

RN 100-42-5 HCA
CN Benzene, ethenyl- (9CI) (CA INDEX NAME)

H₂C CH Ph

RN 25013-15-4 HCA
CN Benzene, ethenylmethyl- (9CI) (CA INDEX NAME)

D1 Me

D1 CH CH₂

IC ICM C07C007-20
CC 35-3 (Chemistry of Synthetic High Polymers)
ST **styrene** polymn inhibitor dihydroxyarene nitroxide hydrogen
transfer agent; **vinyl arom** compd polymn
inhibitor
IT Hydrogen transfer
(agent; **vinyl arom. monomer** polymn.
inhibitor compns. comprising dihydroxyarenes, nitroxides,
hydrogen transfer agent, and optionally org. amines)

- IT Aromatic hydrocarbons, uses
(dihydroxy; **vinyl arom. monomer**
polymn. inhibitor compns. comprising dihydroxyarenes, nitroxides,
hydrogen transfer agent, and optionally org. amines)
- IT Polymerization inhibitors
(**vinyl arom. monomer** polymn.
inhibitor compns. comprising dihydroxyarenes, nitroxides,
hydrogen transfer agent, and optionally org. amines)
- IT Amines, uses
Nitroxides
(**vinyl arom. monomer** polymn.
inhibitor compns. comprising dihydroxyarenes, nitroxides,
hydrogen transfer agent, and optionally org. amines)
- IT **Aromatic compounds**
(**vinyl; vinyl arom. monomer**
polymn. inhibitor compns. comprising dihydroxyarenes, nitroxides,
hydrogen transfer agent, and optionally org. amines)
- IT 86-73-7, Fluorene 91-17-8, Decalin 91-20-3, Naphthalene, uses
91-22-5D, Quinoline, hydro or tetramethylhydro derivs., uses
111-01-3, Squalene 111-02-4, Squalene 119-64-2, Tetralin
120-12-7, Anthracene, uses 613-31-0, 9,10-Dihydroanthracene
(hydrogen transfer agent; **vinyl arom.**
monomer polymn. inhibitor compns. comprising
dihydroxyarenes, nitroxides, hydrogen transfer agent, and
optionally org. amines)
- IT 88-58-4, 2,5-Di-tert-butylhydroquinone 98-29-3,
4-tert-Butylpyrocatechol 111-86-4, n-Octylamine 1948-33-0,
tert-Butylhydroquinone 2226-96-2, 2,2,6,6-Tetramethyl-4-
hydroxypiperidine-1-oxyl 2896-70-0, 2,2,6,6-Tetramethyl-4-
oxopiperidine-1-oxyl
(**vinyl arom. monomer** polymn.
inhibitor compns. comprising dihydroxyarenes, nitroxides,
hydrogen transfer agent, and optionally org. amines)
- IT 100-42-5, **Styrene**, miscellaneous 1321-74-0,
Divinylbenzene, miscellaneous 25013-15-4,
Vinyltoluene 26588-32-9, **Vinylnaphthalene**
(**vinyl arom. monomer** polymn.
inhibitor compns. comprising dihydroxyarenes, nitroxides,
hydrogen transfer agent, and optionally org. amines)

130:237918 The influence of 4-tert-butylcatechol on the emulsion polymerization of **styrene**. Kemmere, M. F.; Mayer, M. J. J.; Meuldijk, J.; Drinkenburg, A. A. H. (Process Development Group, Department of Chemical Engineering, Eindhoven University of Technology, Eindhoven, 5600 MB, Neth.). Journal of Applied Polymer Science, 71(14), 2419-2422 (English) 1999. CODEN: JAPNAB. ISSN: 0021-8995. Publisher: John Wiley & Sons, Inc..

AB The presence of 4-tert-butylcatechol (TBC), a com. autopolymer. inhibitor, in emulsion polymer. of **styrene** affects polymer. process and amt. of formed **polystyrene** particles. TBC strongly enhances radical desorption from the and the particle nu. of the product latex is higher (particle size is smaller) than when polymer. was carried out with distd. **styrene**.

IT 98-29-3, 4-tert-Butylcatechol
(influence of 4-tert-butylcatechol on the emulsion polymer. of **styrene**)

RN 98-29-3 HCA

CN 1,2-Benzenediol, 4-(1,1-dimethylethyl)- (9CI) (CA INDEX NAME)

Bu-t

HO

OH

IT 100-42-5, **Styrene**, reactions
(influence of 4-tert-butylcatechol on the emulsion polymer. of **styrene**)

RN 100-42-5 HCA

CN Benzene, ethenyl- (9CI) (CA INDEX NAME)

H₂C CH Ph

CC 35-3 (Chemistry of Synthetic High Polymers)
ST butylcatechol inhibitor emulsion polymer **styrene**

IT Polymerization
(emulsion; influence of 4-tert-butylcatechol on the emulsion polymer. of **styrene**)

IT Polymerization inhibitors
(influence of 4-tert-butylcatechol on the emulsion polymer. of **styrene**)

IT 1129-21-1, 4-tert-Butyl-1,2-Benzoquinone
(influence of 4-tert-butylcatechol on the emulsion polymer. of **styrene**)

IT 98-29-3, 4-tert-Butylcatechol
(influence of 4-tert-butylcatechol on the emulsion polymer. of **styrene**)

IT 100-42-5, **Styrene**, reactions
(influence of 4-tert-butylcatechol on the emulsion polymer. of **styrene**)

IT 9003-53-6P, **Polystyrene**
(influence of 4-tert-butylcatechol on the emulsion polymer. of **styrene**)

L26 ANSWER 4 OF 14 HCA COPYRIGHT 2002 ACS

111:233873 Inhibition of polymerization of **styrene** in **distillation**. Takahashi, Hideyuki; Suzuki, Shohei; Takahama, Tomohiko; Aoki, Tadamichi; Higaki, Yoshikazu (Mitsubishi Petrochemical Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho JP 01165533 A2 19890629 Heisei, 4 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1987-324832 19871222.

AB A mixt. of a nitrosophenol and p-tert-**butylcatechol** (I) is effective for inhibiting polymn. of **styrene** in **distn.** Thus, **styrene** contg. 100 ppm each of I and 2-methyl-4-nitrosophenol (II) was heated at 110 +/- 0.5.degree. under Ar. Polymer formation was 0.0% after 1 h, 0.13% after 2 h, 0.25% after 3 h, and 0.69% after 4 h vs. 2.0% after 1 h and undeterminable after 2 h for I and 0.0, 0.19, 0.42, and 1.29, resp., for II.

IT 98-29-3, 4-tert-**Butylcatechol**

(polymn. inhibitor, with nitrosophenol, for **styrene**)

RN 98-29-3 HCA

CN 1,2-Benzenediol, 4-(1,1-dimethylethyl)- (9CI) (CA INDEX NAME)

Bu-t

HO

OH

IT 100-42-5, **Styrene**, uses and miscellaneous (polymn. inhibitors for, tert-**butylcatechol** -nitrosophenol mixts. as)

RN 100-42-5 HCA

CN Benzene, ethenyl- (9CI) (CA INDEX NAME)

H₂C CH Ph

IC ICM C07C015-46

ICS C07C007-05; C07C007-20

CC 35-2 (Chemistry of Synthetic High Polymers) Section cross-reference(s): 25

ST nitrosophenol **butylcatechol** inhibitor **styrene** polymn

IT Polymerization inhibitors (tert-**butylcatechol**-nitrosophenol mixts., for **styrene**)

IT 98-29-3, 4-tert-**Butylcatechol**

(polymn. inhibitor, with nitrosophenol, for **styrene**)

IT 6971-38-6, 2-Methyl-4-nitrosophenol

(polymn. inhibitor, with tert-**butylcatechol**, for **styrene**)

- IT 100-42-5, **Styrene**, uses and miscellaneous
(polymn. inhibitors for, tert-**butylcatechol**
-nitrosophenol mixts. as)
- L26 ANSWER 5 OF 14 HCA COPYRIGHT 2002 ACS
108:76405 Polymerizable antioxidants from isocyanatoalkyl esters of
unsaturated carboxylic acids. Johnson, Mark R. (Dow Chemical Co.,
USA). U.S. US 4704470 A 19871103, 5 pp. Cont. of U.S. Ser. No.
298,688, abandoned. (English). CODEN: USXXAM. APPLICATION: US
1984-608631 19840509. PRIORITY: US 1981-298688 19810902.
- AB Addn.-polymerizable antioxidants for polymers are prepd. by reaction
of an isocyanatoalkyl ester of an ethylenically unsatd. carboxylic
acid with an antioxidant having an active H moiety. Thus, a soln.
of 100 g Me 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate in 500
mL PhMe was treated with 21.4 g monoethanolamine at 100.degree. and
refluxed with 1 g MeONa to give 107 g N-(2-hydroxyethyl)-3-(3,5-di-
tert-butyl-4-hydroxyphenyl)propionamide (I). Then, 8 g I and 100 mL
PhMe were refluxed to remove residual moisture by **azeotropic**
distn., cooled to 75.degree., treated with 2 drops
dibutyltin diacetate and 3.78 g to isocyanatoethyl methacrylate to
give a urethane product (II) in 94% yield. A sample of 103.5 g
butadiene-itaconic acid-**styrene** copolymer latex was graft
copolymd. with 0.4 g II in a 50:50 MeOH-**styrene** mixt. in
the presence of Na2S2O8 to give a grafted latex. A film from the
latex was extd. with hexane for 7 h and heated 24 h at 145.degree.
in **air** showing very little yellowing, compared with
significant yellowing for similar film stabilized with 0.75% Ionol
instead of II.
- IC ICM C07C125-04
ICS C07C125-06
- NCL 560137000
- CC 37-3 (Plastics Manufacture and Processing)
Section cross-reference(s): 23, 25
- ST antioxidant tertiary butylhydroxyphenylalkyl methacrylate; butadiene
copolymer grafted antioxidant; itaconic acid copolymer grafted
antioxidant; **styrene** copolymer grafted antioxidant;
hydroxyethylphenylpropionamide isocyanatoethyl methacrylate
- IT 101-54-2D, reaction products with isocyanatoethyl methacrylate
1948-33-0D, tert-Butylhydroquinone, reaction products with
isocyanatoethyl methacrylate 27213-78-1D, tert-
Butylcatechol, reaction products with isocyanatoethyl
methacrylate 30674-80-7D, 2-Isocyanatoethyl methacrylate),
reaction products with substituted phenols and thiols and amines
(antioxidants, polymerizable)
- L26 ANSWER 6 OF 14 HCA COPYRIGHT 2002 ACS
101:24157 Separation of alkenylbenzene **monomers**. (Nippon Steel
Chemical Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho JP 59029624 A2
19840216 Showa, 5 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP
1982-138577 19820811.
- AB Polymn. of alkenylbenzene **monomers** contained in a
hydrocarbon mixt. during **distn.** is avoided by use of

100-1000 ppm N-nitroso compd. and 5-100 ppm catechol compd. Thus, 10 mL ethylbenzene dehydrogenation product contg. 4.52 g **styrene** [100-42-5], 300 ppm N-nitrosodiphenylamine [86-30-6], and 80 ppm p-tert-**butylcatechol** (I) [98-29-3] was **distd.** at 105.degree. and reduced pressure under N for 2 h. The residue did not contain polymer, whereas a control contg. no I gave a residue with 0.03 g polymer.

IT 100-42-5P, preparation
(**distn.** of, in presence of **butylcatechol** and nitrosodiphenylamine)

RN 100-42-5 HCA

CN Benzene, ethenyl- (9CI) (CA INDEX NAME)

H₂C CH Ph

IT 98-29-3
(**styrene distn.** in presence of nitrosodiphenylamine and)

RN 98-29-3 HCA

CN 1,2-Benzenediol, 4-(1,1-dimethylethyl)- (9CI) (CA INDEX NAME)

Bu-t

HO

OH

IC C07C007-05; C07C015-44

CC 35-10 (Chemistry of Synthetic High Polymers)

ST nitrosodiphenylamine **styrene distn.**;
butylcatechol styrene distn

IT Polymerization inhibitors
(nitrosodiphenylamine, with **butylcatechol**, for **distn.** of **styrene**)

IT 100-41-4DP, dehydrogenation products 100-42-5P, preparation
(**distn.** of, in presence of **butylcatechol** and nitrosodiphenylamine)

IT 86-30-6
(polymn. inhibitors, in **distn.** of **styrene**)

IT 98-29-3
(**styrene distn.** in presence of nitrosodiphenylamine and)

L26 ANSWER 7 OF 14 HCA COPYRIGHT 2002 ACS

92:96170 **Distillation** of **vinyl aromatic**

compounds using polymerization inhibitors with low volatility.

Watson, James M. (Cosden Technology, Inc., USA). U.S. US 4177110 19791204, 9 pp. (English). CODEN: USXXAM. APPLICATION: US 1978-925817 19780718.

AB Methods are presented for sepg. C₆H₆-PhMe-**styrene**-ethylbenzene mixts. in 3-column systems with the combination of phenothiazine and tert-**butylcatechol** as the polymn. inhibitor. In 1 method, the crude **styrene** is fed into the 1st column, along with the inhibitor in a hydrocarbon diluent (for decreasing the viscosity of the bottom product. C₆H₆ and PhMe are taken overhead and the **styrene**-ethylbenzene-inhibitor-tar-diluent bottom product is fed to the 2nd column. More inhibitor, in ethylbenzene, is fed into the upper part of the 2nd column. Ethylbenzene is taken overhead. The 2nd bottom product is fed into the 3rd column, from which **styrene** is taken overhead with purity >97%. **Air** is fed into the reboiling circuit of all of the columns. In the 2nd method, the crude **styrene** is fed into a column, a C₆H₆-PhMe-ethylbenzene mixt. is taken overhead and fed into a 2nd column, and the bottom product is fed into a 3rd column for **styrene** recovery. The inhibitor in ethylbenzene is fed into the top of the 1st column. **Air** is fed into the reboiler circuit of the 1st and 3rd columns. A diluent is fed into the reboiler circuit of the 1st column.

IT 100-42-5P, preparation
(distn. of)

RN 100-42-5 HCA

CN Benzene, ethenyl- (9CI) (CA INDEX NAME)

H₂C CH Ph

IC B01D003-34; C07C007-18

NCL 203009000

CC 48-1 (Unit Operations and Processes)

Section cross-reference(s): 25, 35

ST **styrene distn**

IT 100-42-5P, preparation
(distn. of)

L26 ANSWER 8 OF 14 HCA COPYRIGHT 2002 ACS

89:44404 **Distillation** of easily polymerizable **aromatic**

vinyl compounds. Watson, James M. (Cosden Technology, Inc., USA). Ger. Offen. DE 2707074 19771013, 20 pp. (German). CODEN: GWXXBX. APPLICATION: DE 1977-2707074 19770218.

AB A synergistic inhibitor system for avoiding undesirable polymn. in **distn.** of **vinylarom.** compds., e.g., **styrene** (I) [100-42-5], under a wide range of pressure and temp. contains phenothiazine (II) [92-84-2] 5-200, tert-**butylcatechol** (III) [27213-78-1] 1-100, and optionally nitrosodiphenylamine [86-30-6] 25-200 ppm, depending on **distn.** conditions. The preferred **distn.** temp. is 90-143.degree. and **distn.** is carried out at atm. or reduced pressure. When vacuum **distn.** is used, 0 or

air must be added or no inhibiting effect is obtained.

Thus, 50 g I was heated at 115.degree. +/- 1.degree. in presence of 100 ppm II and 10 ppm III to give an inhibition time of 4-4.5 h as compared with 1-1.5 h or <0.5 h with II or III, resp.

IT 100-42-5P, preparation
(**distn.** of, polymn. inhibitors for, phenothiazine-tert-
butylcatechol-nitrosodiphenylamine as)

RN 100-42-5 HCA

CN Benzene, ethenyl- (9CI) (CA INDEX NAME)

H2C CH Ph

IC C07C015-10

CC 35-2 (Synthetic High Polymers)

ST phenothiazine polymn inhibitor **styrene**;
butylcatechol polymn inhibitor **styrene**;
nitrosodiphenylamine polymn inhibitor **styrene**; vinyl compd
polymn inhibitor; **arom vinyl** monomer polymn
inhibitor; **distn** vinyl monomer polymn inhibitor

IT Polymerization inhibitors
(phenothiazine-tert-**butylcatechol**-nitrosodiphenylamine,
for **distn.** of **styrene**)

IT **Vinyl** compounds, preparation
(**arom.**, **distn.** of, synergistic polymn.
inhibitors for)

IT **Aromatic** compounds
(**vinyl**, **distn.** of, synergistic polymn.
inhibitors for)

IT 100-42-5P, preparation
(**distn.** of, polymn. inhibitors for, phenothiazine-tert-
butylcatechol-nitrosodiphenylamine as)

IT 27213-78-1
(polymn. inhibitors, with phenothiazine and nitrosodiphenylamine,
for **distn.** of **styrene**)

IT 86-30-6
(polymn. inhibitors, with phenothiazine and tert-
butylcatechol, for **distn.** of **styrene**)

IT 92-84-2
(polymn. inhibitors, with tert-**butylcatechol** and
nitrosodiphenylamine, for **distn.** of **styrene**)

L26 ANSWER 9 OF 14 HCA COPYRIGHT 2002 ACS

83:11238 Ion exchangers. XVI. Removal of inhibitors from
monomers on ion exchangers. Kolarz, Bozena; Gozdz, Antoni;
Trochimczuk, Witold (Inst. Technol. Org. Tworzyw Sztucznych,
Politech. Wroclaw, Wroclaw, Pol.). Polimery (Warsaw), 19(9), 417-21
(Polish) 1974. CODEN: POLIA4.

AB Best results in removal of hydroquinone [123-31-9] from
styrene (I) [100-42-5] and of p-tert-
butylpyrocatechol [98-29-3] from divinylbenzene
[1321-74-0] were obtained by sorption on strongly basic,

macroreticular anion exchangers Wofatit EA-60 (II) [9063-61-0] and Varion AT-400 (III) [9081-62-3] in their OH forms. Utilization of the exchangers in a dynamic method was 6-8 times better than in a static one. Desorption of the inhibitors from II or III was little changed with progressing cycles of **monomer** purification. I purified by the conventional extn.-**distn.** polymd. .apprx.3 times slower than I purified with anion exchangers.

IT 100-42-5P, preparation
(inhibitor removal from, anion exchangers for)
RN 100-42-5 HCA
CN Benzene, ethenyl- (9CI) (CA INDEX NAME)

H₂C CH Ph

IT 98-29-3
(removal of, from divinylbenzene, anion exchangers for)
RN 98-29-3 HCA
CN 1,2-Benzenediol, 4-(1,1-dimethylethyl)- (9CI) (CA INDEX NAME)

Bu-t

HO

OH

CC 36-2 (Plastics Manufacture and Processing)
ST inhibitor removal vinyl **monomer**; **styrene** removal
hydroquinone; vinylbenzene removal butylpyrocatechol; anion
exchanger **monomer** purifn
IT Kinetics of polymerization
(of **styrene**, effect of inhibitor removal method on)
IT Anion exchangers
(phenol inhibitors removal by, from vinyl **monomers**)
IT 9063-61-0 9081-62-3
(anion exchangers, butylpyrocatechol and hydroquinone removal
from **styrene** and divinylbenzene by)
IT 11108-60-4 37311-41-4 39434-92-9 55819-36-8
(anion exchangers, hydroquinone removal from **styrene**
by)
IT 100-42-5P, preparation 1321-74-0P, preparation
(inhibitor removal from, anion exchangers for)
IT 98-29-3
(removal of, from divinylbenzene, anion exchangers for)
IT 123-31-9, uses and miscellaneous
(removal of, from **styrene**, anion exchangers for)

L26 ANSWER 10 OF 14 HCA COPYRIGHT 2002 ACS
83:11138 **Styrene** separation from naphtha pyrolyzate.

Watanabe, Yoshihiro; Sakamoto, Sukehiko; Takeda, Hideichi (Sumitomo Chemical Co., Ltd., Japan). Japan. Kokai JP 50004025 19750116 Showa, 3 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1973-55285 19730517.

AB Polymn. inhibitors were used to prevent **styrene** [100-42-5] loss during extractive **distn.** with hexamethylphosphoramide [680-31-9] from C5-9 hydrocarbons. Thus, a 23:77 **styrene**-(Me₂N)₃PO mixt. contg. 1000 ppm S [7704-34-9] or NaNO₂ [7632-00-0] was heated 3 hr at 120.degree. with <0.1% **styrene** loss compared to 19% polymn. without inhibitor. Heating in AcNMe₂ contg. 1000 ppm NaNO₂ resulted in 3.9% loss. A C8 arom. fraction from naphtha pyrolysis was extd. with (Me₂N)₃PO contg. 500 ppm S in a packed column at 135.degree. bottom temp., resulting in **styrene** recovery with no loss.

IT 98-29-3
(polymn. inhibitors, in extractive **distn.** of **styrene** from naphtha cracking products)

RN 98-29-3 HCA

CN 1,2-Benzenediol, 4-(1,1-dimethylethyl)- (9CI) (CA INDEX NAME)

Bu-t

HO

OH

IT 100-42-5P, preparation
(recovery of, from naphtha cracking products, by extractive **distn.**)

RN 100-42-5 HCA

CN Benzene, ethenyl- (9CI) (CA INDEX NAME)

H₂C CH Ph

NCL 16C1

CC 35-2 (Synthetic High Polymers)
Section cross-reference(s): 25, 51

ST **styrene** recovery naphtha cracking; phosphoramid
hexamethyl extractive **distn.**; **styrene** polymn
inhibitor; extractive **distn** **styrene**

IT Naphtha
(cracking products, extractive **distn.** of **styrene** from)

IT Polymerization inhibitors
(in extractive **distn.** of **styrene** from naphtha
cracking products)

IT 680-31-9
(in extractive **distn.** of **styrene** from naphtha

cracking products)
IT 86-30-6 **98-29-3** 123-31-9, uses and miscellaneous
7632-00-0 7704-34-9, uses and miscellaneous
(polymn. inhibitors, in extractive **distn.** of
styrene from naphtha cracking products)
IT 100-42-5P, preparation
(recovery of, from naphtha cracking products, by extractive
distn.)

L26 ANSWER 11 OF 14 HCA COPYRIGHT 2002 ACS

66:104754 Stabilization of **styrene** during storage. Kovrizhko,
L. F.; Raevskii, A. B.; Ivanova, Z. V. Tr. Lab. Khim. Vysokomol.
Soedin., Voronezh. Gos. Univ. , No. 3 72-7 From: Ref. Zh., Khim.
1966, Pt. II, Abstr. No. 23N193 (Russian) 1964. CODEN: TKVVA7.
AB p-tert-Butylpyrocatechol (I), hydroquinone (II),
p-hydroxydiphenylamine (III), and 2,5-di-tert-butylhydroquinone (IV)
were studied as inhibitors for stabilization of **styrene**
(V) during storage and transportation. Freshly **distd.**
tech. grade V was placed in an **air atm.** or
O-free N in a glass ampul contg. Al shavings (160 sq. cm.
Al surface/100 g. V) and left to stand. Then the contents of
peroxides, aldehydes, and polymer in V were detd. and the
permissible storage times of V in the presence of the given
inhibitor was calcd. on the principle that com. V should contain
<0.02% aldehydes and <0.005% peroxides and should not contain
polymers (given are: inhibitor, amt. in wt. %, temp., permissible
storage times of V in N and **air**, resp., in days): I,
0.0005, .apprx.20.degree., 150, 150; I, 0.005, .apprx.20.degree.,
>180, >180; I, 0.01, .apprx.20.degree., >180, >180; I, 0.05,
.apprx.20.degree., >180, >180; III, 0.01, .apprx.20.degree., >180,
>180; III, 0.05, .apprx.20.degree., >180, >180; I, 0.01, 40.degree.,
90, 90; I, 0.05, 40.degree., >120, >120; III, 0.01, 40.degree., 45,
35; III, 0.05, 40.degree., 45, 35; II, 0.01, 40.degree., 15, 15; II,
0.05, 40.degree., 25, 15; S, 0.05, 40.degree., <5, <5; IV, 0.05,
40.degree., <5, <5. II in the presence of Cu was more effective as
a stabilizer.
IT **98-29-3**
(as stabilizer for **styrene**)
RN 98-29-3 HCA
CN 1,2-Benzenediol, 4-(1,1-dimethylethyl)- (9CI) (CA INDEX NAME)

Bu-t

HO

OH

IT 100-42-5, reactions
(stabilization of)

RN 100-42-5 HCA
CN Benzene, ethenyl- (9CI) (CA INDEX NAME)

H₂C CH Ph

CC 25 (Noncondensed Aromatic Compounds)
IT 123-31-9, uses and miscellaneous
(as stabilizer for **styrene**)
IT 88-58-4 98-29-3
(as stabilizer for **styrene**)
IT 100-42-5, reactions
(stabilization of)

L26 ANSWER 12 OF 14 HCA COPYRIGHT 2002 ACS

61:4795 Original Reference No. 61:794e-g Vinylbenzyl monoepoxide ether and thio ether and their resins. De Lano, Wendell N. (Dow Chemical Co.). US 3127382 19640331, 3 pp. (Unavailable). APPLICATION: US 19611220.

AB The above monomer (I) and its thio ether analog, their homopolymers, their copolymers with ethylenically unsatd. monomers, such as **styrene**, vinyltoluene, acrylonitrile, or acrylic acid, and resins obtained by reaction of the polymers with curing agents, such as phthalic anhydride, phenols, polyphenols, and amines, are described. To prep. I, 40 g. 50% aq. NaOH was added in a 15 min. period to a stirring mixt. of 67 g. mixed o- and p-vinylbenzyl alc., 185 g. epichlorohydrin, and 0.07 g. tert-**butylcatechol**. The reaction mass was stirred for an addnl. 1 hr. and 45 min. and then sepd. into an oil phase and aq. phase. **Distn.** of the oil phase at 100.degree. (0.4 mm.) gave a product contg. over 80% I. Purification by chromatographic sepn. gave a sample contg. 46.0% para isomer, 51.4% ortho isomer, and 1.6% other materials, n_{25D} 1.5440, d₂₅₄ 1.0580. The para isomer had n_{25D} 1.5449. Two ml. unpurified I, 10 ml. **styrene**, and 0.2 ml. Bz202 were mixed and heated at 100.degree. for 72 hrs. The resulting copolymer, dissolved in 50 ml. toluene, contained 4.2% oxirane groups. In sep. reactions, the polymer soln. reacted with the amts. of phthalic anhydride and dicyandiamide (as hardening agents) required to react with the oxirane groups present. The solns. either gelled or thickened after heating at 100.degree. for 50 min. followed by 6 hrs. at 150.degree.. After addnl. time in **air**, the gelled resins cured to hard, resinous solids. This compn., i.e. the resin in toluene, is esp. useful as a liquid coating compn. which rapidly loses toluene and cures to a hard, durable film.

NCL 260088300

CC 48 (Plastics Technology)

L26 ANSWER 13 OF 14 HCA COPYRIGHT 2002 ACS

59:29392 Original Reference No. 59:5366e-f Resinous coating compositions. Mueller, Albert C.; Tess, Roy W. H. (Shell Oil Co.). US 3095389 19630625, 5 pp. (Unavailable). APPLICATION: US 19580630.

AB Copolymers prep'd. from an alkenol and an alkenylbenzene, or an alkene oxide adduct of the prep'd. copolymer, are mixed with shellac and the resulting mixts. are dissolved in alc. to give coating compns. which have fast drying rates and are resistant to H₂O. Thus, 11,085 parts allyl alc., 994 parts **styrene** contg. 0.005% tert-**butylcatechol** stabilizer, and 241.6 parts (tert-Bu)₂O₂ are heated at 135.degree. for 5 hrs. as addnl, **styrene** is pumped into the autoclave, the unreacted monomers are **distd.**, and a brittle low polymer is obtained. A mixt. contg. 70% prep'd. copolymer and 30% shellac is dissolved in EtOH to give a 40% soln., the soln. is spread on Sn panels, and the coating is **air** dried in approx. 30 min. to give hard coatings, dry time to cotton-free state 20 min., hardness (Tukar hardness test, Knoop no.) 9.1, 3-day-old film immersed in H₂O for 1 hr., no effect.

NCL 260008000

CC 52 (Coatings, Inks, and Related Products)

IT Allyl alcohol, polymers with **styrene**, adducts with acid anhydrides
(coatings from shellac and, for metals)

L26 ANSWER 14 OF 14 HCA COPYRIGHT 2002 ACS

48:7100 Original Reference No. 48:1294b-i,1295a-g The synthesis and polymerization of some fluorinated **styrenes**. Prober, Maurice (General Elec. Co., Schenectady, NY). J. Am. Chem. Soc., 75, 968-73 (Unavailable) 1953.

GI For diagram(s), see printed CA Issue.

AB A series of fluorinated **styrenes**, PhCF:CF₂ (I), PhCH:CF₂ (II), PhCF:CHF (III), and PhCCl:CHF (IV) was prep'd. starting with CHF₂CO₂Na. I was also prep'd. by the direct reaction of C₂ClF₃ and C₆H₆. I gave a polymer which softens at high temp. CHF₂CO₂Na treated with concd. H₂SO₄ and the acid heated with excess BzCl yielded 83% CHF₂COCl, b₇₅₃ 28-8.3.degree.; also obtained in 65% yield directly from CHF₂CO₂K with BzCl. PhCOCHF₂ (V), b₃₀ 86-7.degree., b₇₅₄ 185-6.degree., m. 9.degree., n_{20D} 1.4982, was obtained in 69% yield by the method of Cohen, et al. (C.A. 44, 2462g). V treated with 10% excess PCl₃, followed by vigorous stirring with H₂O yielded 91% PhCCl₂CHF₂ (VI), b₃₀ 107-8.degree., b₇₅₃ 211-12.degree., m. -13.degree., n_{20D} 1.5086, d₂₀ 1.384. VI (76.5 g.) and 21.6 g. SbF₃ heated at 220-30.degree., and the **distillate**, b. 185-90.degree., washed with dil. HCl and H₂O, dried with CaCl₂, and rectified gave 1.9 g. PhCF₂CHF₂ (VII), 37.5 g. PhCClFCHF₂ (VIII), b₅₅ 92-4.degree., b₇₆₃ 173-4.degree., n_{20D} 1.4686, d₂₀ 1.328, and 23.5 g. recovered VI. VI (105.6 g.), 29.9 g. SbF₃, 2.9 g. SbCl₅, and 100 cc. CCl₂FCClF₂ (IX) refluxed 6 hrs. with stirring, the IX soln. decanted off, the solid washed with fresh IX, and the combined IX soln. washed with dil. HCl and H₂O, dried, and rectified gave 28.8 g. (32%) VII (b₆₀₋₁ 67-8.degree., b₇₅₆ 139-40.degree., n_{20D} 1.4258, d₂₀ 1.277), 11.1 g. VIII, and 21.2 g. VI. IX did not undergo dehydrohalogenation with quinoline, aq. KOH, molten NaOH, or KI-ZnAcNH₂. To 40.7 g. NaOH (contg. 2% H₂O) was added dropwise at 230-50.degree. 33.0 g. VIII, the

distillate dild. with IX, and the soln. dried with CaCl_2 and rectified (tert-**butylcatechol** added to still-pot) to yield 3.4 g. I, b70 67-8.degree., n20D 1.4731, and 7.9 g. VIII. VI (42.2 g.), 26.1 g. Zn dust and 200 cc. dry dioxane refluxed 7 hrs. with stirring, the mixt. steam-**distd.**, the aq. soln. extd. with CHCl_3 , and the ext. combined with the org. phase, dried with CaSO_4 , and rectified gave 16.4 g. (52%) IV, b29 93-4.degree., n20D 1.5401. VIII (38.9 g.), 52.2 g. Zn dust, and 180 cc. dry dioxane gave similarly in 27 hrs. 11.5 g. (41%) III, b60 88-90.degree., n20D 1.5061, polymerized on long standing at room temp. V (88.0 g.), 0.353 mole (iso- PrO) $_3\text{Al}$, and 480 cc. iso- PrOH refluxed 5.5 hrs. under a short column, 280 cc. **distillate** collected, the excess iso- PrOH removed in vacuo, the sirupy residue hydrolyzed with dil. HCl and the aq. soln. extd. with Et_2O gave 80.0 g. (90%) PhCH(OH)CHF_2 (X), b19-20 107-8.degree., b758 212-13.degree., n20D 1.4942. X (78.5 g.) and 47.2 g. AcCl heated 4 hrs. at 110.degree., the mixt. washed with dil. aq. KOH , then with H_2O , dried, and rectified yielded 87.8 g. (88%) acetate of X, b20 114-16.degree., b758 225-7.degree., n20D 1.4715. X (146.3 g.) and 143 g. heated 2 hrs. at 140.degree. yielded 228.0 g. (94%) benzoate (XI) of X, b6.3 161-3.degree., n20D 1.5361, m. 48-9.degree. (from heptane). XI (171.6 g.) was passed during 7 hrs. through a Pyrex packed tube (58 .times. 2 cm.) of which a 38-cm. section was heated at 625-36.degree., the reaction product washed with dil. base, dried, and **distd.** in vacuo to yield 8.8 g. (10%) II (b61-2 65-6.degree., n20D 1.4925), 9.1 g. V (b30 84-7.degree., n20D 1.4978), and 42.2 g. unreacted XI. Through an unpacked 78 .times. 2-cm. Pyrex tube heated over a 30-cm. section to 550.degree. and swept out previously with dry N were passed in 4.5 hrs. 234 g. C_2ClF_3 (scrubbed by H_2SO_4) and 117.9 g. C_6H_6 to give in an attached water-cooled trap 163.6 g., and in a subsequent Dry Ice trap 172.6 g. condensate, resp. The Dry Ice condensate was **distd.** through aq. KOH , dried over CaCl_2 , recondensed, and rectified to give crude dichlorotetrafluoropropene (XII), C_2ClF_3 , and chloropentafluoropropene (XIII); the residue was combined with the water-trap condensate, the mixt. dild. with CH_2Cl_2 , washed with dil. aq. KOH , and rectified to give CH_2Cl_2 ; C_6H_6 ; 8.4 g. I, b70 66.2-7.5.degree., n20D 1.4732, m. -24 to -23.degree.; dimeric I, b6 120-1.degree., n20D 1.4973; the following compds. believed to arise from the dehydrochlorination involving C_6H_6 and the allylic Cl of the chlorofluoroolefins formed by the pyrolysis of C_2ClF_3 : pentafluorophenylpropene, b70 81-4.degree., n20D 1.4428, chlorotetrafluorophenylpropene, b70 99-102.degree., n20D 1.4620, and chlorohexafluorophenylbutene, b70 108-10.degree., n20D 1.4418 (1 g. of each oxidized with $\text{K}_2\text{Cr}_2\text{O}_7$ gave 0.26, 0.22, and 0.19 g. BzOH , resp.); Ph_2 , b10 114-17.degree.; CHF:CF_2 , b. -61 to 60.degree. (dibromide, b. 74-5.degree.); XIII, b. 8-9.degree. (identified as $\text{C}_3\text{Cl}_3\text{F}_5$, b73.degree., n20D 1.3510); XII, b100 -1 to 0.degree., b. 46-8.degree., n20D 1.3520; $\text{CF}_2.\text{CF}_2.\text{CClF.CClF}$, b. 59-60.degree., n20D 1.3348; and dichlorohexafluorobutene, b100 14-15.degree., b. 66-7.degree. [identified as $(\text{CClFCClF}_2)_2$, b. 133-4.degree., n20D 1.3844]. I (1 g.) refluxed 2 hrs. with 2.0 g. $\text{K}_2\text{Cr}_2\text{O}_7$ in 20 cc. H_2O

and 10 cc. H₂SO₄, the soln. extd. with Et₂O, the ext. shaken with aq. KOH, and the basic soln. acidified gave 0.34 g. BzOH, m. 121-2.degree.. Bulk polymerization of the **fluorostyrenes** was carried out for 72 hrs. with Bz₂O₂ at 70-5.degree. and with BF₃ at 1-4.degree.; the BF₃ was measured volumetrically and condensed in the polymerization tube with liquid N; the polymer was pptd. with MeOH and dried in an oven. The % yield of polymer at the catalyst concn. indicated, and the softening points of the polymer are for: I, 9.7, 2.9% Bz₂O₂, 185-90.degree.; 0, 1.2% BF₃, -; II, 0.4, 3.5% Bz₂O₂, 176-80.degree.; 0.4, 2.4% BF₃, 127-30.degree.; III, 0.7, 2.7% Bz₂O₂, -; 39, 2.8% BF₃, 225-30.degree. (strong decompn.); and IV, 0, 2.7% Bz₂O₂, -; 0, 3.2% BF₃, -. Bulk polymerizations of I with 0.3% of the following catalysts were carried out for 72 hrs. (reaction temp. and % yield of polymer given): Bz₂O₂, 65-8.degree., 6.2; azobisisobutyronitrile (XIV), 65-8.degree., 3.5; ultraviolet light and XIV, 45-50.degree., 4.0%; Me₃COOH, 81-3.degree., 4.3%; BzO₂CMe₃ (XV), 101-4.degree., 0.7%; (Me₃CO)₂, 120-3.degree., 6.4%; the softening points of these polymers were in the range 210-25.degree.; the MeOH-sol. polymers from these runs were obtained by heating the mixt. at 75.degree. in a high vacuum; the yields of dimeric I in the runs with Bz₂O₂ and XV were 50 and 85%, resp. The emulsion polymerizations of I were carried out by **distg.** in a vacuum system into 2 cc. degassed aq. soln. contg. 0.040 g. emulsifier and 0.0015 g. K₂S₂O₈, shaking the mixt. in a sealed tube 72 hrs. at 50-5.degree. and pptg. the polymer with MeOH; Ivory soap (XVI), Aerosol OT (XVII), and Cl₂H₂₅NH₂.HCl (XVIII) gave thus 67, 47, and 83% conversion, resp.; to polymers with softening points at 240-5.degree. (with XVI and XVII), and a clear point at 237.degree. (with XVIII). The polymeric I was sol. in aromatic solvents; transparent films were cast from PhMe solns.; the intrinsic viscosity in PhMe (0.1-0.2 g./100 cc.) was 1.0 at 20.degree., corresponding probably to a mol. wt. of 100000-500000. Strips of polymer heat aged 30 days at 150-3.degree., 175-80.degree., and 200-5.degree. in circulating **air**-ovens had not discolored, fused, or become more brittle. Heat aging of powd. polymer for 33 days under N at 225-30.degree. gave 0.7% wt. loss, and some cross-linking as evidenced by the incomplete soly. in excess PhMe. The dielec. const. and power factor were run on a 5-mil sheet; the results are illustrated by a graph. Similar emulsion polymerizations of II were carried out (% conversion, and softening point of polymer given) with: XVI, 3.5, 207-11.degree.; XVII, 2.8, 208-13.degree.; and XVIII, 7.3, 220-5.degree..

CC 10 (Organic Chemistry)

=> d 125 1-31 cbib abs hitind

L25 ANSWER 1 OF 31 HCA COPYRIGHT 2002 ACS

124:9653 Inhibiting polymerization of vinyl compounds. Yasuda, Minoru; Moriya, Osamu; Shigematsu, Kunihiro (Sumitomo Chemical Co. Ltd., Japan). Brit. UK Pat. Appl. GB 2285983 A1 19950802, 22 pp. (English). CODEN: BAXXDU. APPLICATION: GB 1995-1046 19950119.

PRIORITY: JP 1994-6465 19940125.

AB Polymn. of a vinyl compd. during **distn.** is inhibited by adding (1) phenothiazine, hydroquinone, p-methoxyphenol, cresol, phenol, tert-**butylcatechol**, diphenylamine, or methylene blue, (2) a copper dithiocarbamate compd., and (3) a metal, an alloy contg. the metal (.gtoreq.90% by wt.), an acetate of the metal, or an oxide of the metal, where the metal is Cr, Mg, Ti, or Co.

IC ICM C07C051-50

CC 35-3 (Chemistry of Synthetic High Polymers)

IT **Distillation**

(inhibiting polymn. of vinyl compds. during **distn.**)

IT Vinyl compounds, miscellaneous

(inhibiting polymn. of vinyl compds. during **distn.**)

IT 61-73-4, Methylene blue 92-84-2, Phenothiazine 108-95-2, Phenol, uses 122-39-4, Diphenylamine, uses 123-31-9, Hydroquinone, uses 142-72-3, Magnesium acetate 150-76-5, p-Methoxyphenol 1319-77-3, Cresol 7440-32-6, Titanium, uses 13463-67-7, Titanium dioxide, uses 13927-71-4, Copper dibutylldithiocarbamate 27213-78-1, tert-**Butylcatechol**

(polymn. inhibitors contg.)

IT 79-10-7, Acrylic acid, miscellaneous 79-10-7D, Acrylic acid, esters 79-41-4, Methacrylic acid, miscellaneous 79-41-4D, Methacrylic acid, esters **100-42-5**, **Styrene**, miscellaneous 107-13-1, Acrylonitrile, miscellaneous

(polymn. inhibitors for)

L25 ANSWER 2 OF 31 HCA COPYRIGHT 2002 ACS

123:143336 Preparation of alkenylcyclohexenes by dimerization of conjugated dienes. Iwamasa, Kenji; Matsuoka, Hideto; Tsukamoto, Koji; Kaneda, Mitsuhiro; Inoki, Satoru; Hashimoto, Isao (Mitsui Petrochemical Ind, Japan). Jpn. Kokai Tokkyo Koho JP 07048288 A2 19950221 Heisei, 5 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1993-191386 19930802.

AB Alkenylcyclohexenes, useful as materials for **styrene** and ethylbenzene, are prepd. by heating C4-6 chain-type conjugated dienes in the presence of monovalent Cu compds. having (perfluoro)alkylsulfoxy ion, arylsulfoxy ion, tetrafluoroborate ion, tetraphenylborate ion, and/or hexafluorophosphate ion. C4 **distillate** contg. 1,3-butadiene was autoclaved with Cu(I) trifluoromethanesulfonate-C6H6 complex and tert-**butylcatechol** in mesitylene at 180.degree. for 3 h to give 62% 4-vinylcyclohexene, vs. 21%, without the catalyst.

IC ICM C07C013-20

ICS B01J031-22; C07C002-46

ICA C07B061-00

CC 24-5 (Alicyclic Compounds)

ST alkenylcyclohexene prepn intermediate **styrene**

ethylbenzene; copper catalyst dimerization conjugated diene; cyclization conjugated diene catalyst copper

IT Alkadienes

(prepn. of alkenylcyclohexenes as intermediates for **styrene** and ethylbenzene from C4-6 conjugated dienes by

- using Cu(I) compds. as catalysts)
- IT Dimerization catalysts
Ring closure catalysts
(prepn. of alkenylcyclohexenes as intermediates for **styrene** and ethylbenzene from conjugated dienes by using Cu(I) compds. as catalysts)
- IT 71-43-2D, Benzene, copper complexes 75-05-8D, Acetonitrile, copper complexes 7440-50-8D, Copper, complexes with benzene or acetonitrile
(prepn. of alkenylcyclohexenes as intermediates for **styrene** and ethylbenzene from conjugated dienes by using Cu(I) compds. as catalysts)
- IT 100-41-4P, Ethylbenzene, preparation **100-42-5P, Styrene**, preparation
(prepn. of alkenylcyclohexenes as intermediates for **styrene** and ethylbenzene from conjugated dienes by using Cu(I) compds. as catalysts)
- IT 106-99-0, 1,3-Butadiene, reactions
(prepn. of alkenylcyclohexenes as intermediates for **styrene** and ethylbenzene from conjugated dienes by using Cu(I) compds. as catalysts)
- IT 100-40-3P, 4-Vinylcyclohexene
(prepn. of alkenylcyclohexenes as intermediates for **styrene** and ethylbenzene from conjugated dienes by using Cu(I) compds. as catalysts)
- L25 ANSWER 3 OF 31 HCA COPYRIGHT 2002 ACS
- 123:9093 Preparation of alkenylcyclohexenes by dimerization of conjugated dienes. Kaneda, Mitsuhiro; Matsuoka, Hideto; Iwamasa, Kenji; Tsukamoto, Koji; Inoki, Satoru; Ookawa, Katsuo; Hashimoto, Isao (Mitsui Petrochemical Ind, Japan). Jpn. Kokai Tokkyo Koho JP 07048289 A2 19950221 Heisei, 5 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1993-191387 19930802.
- AB Alkenylcyclohexenes, useful as materials for **styrene** and ethylbenzene, are prepd. by heating C4-6 chain-type conjugated dienes in the presence of divalent Cu compds. and carboxylic acids at 160-210.degree.. C4 **distillate** contg. 1,3-butadiene was autoclaved with Cu(AcO)2, AcOH, and tert-**butylcatechol** at 180.degree. for 3 h to give 49% 4-vinylcyclohexene, vs. 18%, without the catalyst.
- IC ICM C07C013-20
ICS B01J031-04; B01J031-22; C07C002-46
- ICA C07B061-00
- CC 24-5 (Alicyclic Compounds)
- ST alkenylcyclohexene prepn intermediate **styrene** ethylbenzene; copper catalyst dimerization conjugated diene; cyclization conjugated diene catalyst carboxylate
- IT Alkadienes
(prepn. of alkenylcyclohexenes as intermediates for **styrene** and ethylbenzene from C4-6 conjugated dienes by using Cu(II) compds. and carboxylic acids)
- IT Dimerization catalysts

Ring closure catalysts

(prepn. of alkenylcyclohexenes as intermediates for **styrene** and ethylbenzene from conjugated dienes by using Cu(II) compds. and carboxylic acids)

IT Carboxylic acids, uses

(prepn. of alkenylcyclohexenes as intermediates for **styrene** and ethylbenzene from conjugated dienes by using Cu(II) compds. and carboxylic acids)

IT 64-19-7, Acetic acid, uses 85-52-9, 2-Benzoylbenzoic acid
142-71-2, Cupric acetate 552-16-9, 2-Nitrobenzoic acid
1317-38-0, Cupric oxide, uses 1466-76-8, 2,6-Dimethoxybenzoic acid
7758-98-7, Cupric sulfate, uses 13395-16-9, Cupric
bis(2,4-pentanedionate)

(prepn. of alkenylcyclohexenes as intermediates for **styrene** and ethylbenzene from conjugated dienes by using Cu(II) compds. and carboxylic acids)

IT 100-41-4P, Ethylbenzene, preparation **100-42-5P**,
Styrene, preparation

(prepn. of alkenylcyclohexenes as intermediates for **styrene** and ethylbenzene from conjugated dienes by using Cu(II) compds. and carboxylic acids)

IT 106-99-0, 1,3-Butadiene, reactions

(prepn. of alkenylcyclohexenes as intermediates for **styrene** and ethylbenzene from conjugated dienes by using Cu(II) compds. and carboxylic acids)

IT 100-40-3P, 4-Vinylcyclohexene

(prepn. of alkenylcyclohexenes as intermediates for **styrene** and ethylbenzene from conjugated dienes by using Cu(II) compds. and carboxylic acids)

L25 ANSWER 4 OF 31 HCA COPYRIGHT 2002 ACS

122:290372 Preparation of alkenylcyclohexenes by dimerization of conjugated dienes. Matsuoka, Hideto; Kaneda, Mitsuhiro; Tsukamoto, Koji; Iwamasa, Kenji; Inoki, Satoru; Hashimoto, Isao (Mitsui Petrochemical Ind, Japan). Jpn. Kokai Tokkyo Koho JP 07048290 A2 19950221 Heisei, 5 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1993-191388 19930802.

AB Alkenylcyclohexenes, useful as materials for **styrene** and ethylbenzene, are prepd. by heating C4-6 chain-type conjugated dienes in the presence of monovalent Cu compds. and arom. carboxylic acids as acidic org. compds. C4 **distillate** contg. 1,3-butadiene was autoclaved with Cu₂O, 2-benzoylbenzoic acid, and tert-**butylcatechol** in PhOH at 180.degree. for 3 h to give 75% 4-vinylcyclohexene, vs. 33%, without the acid.

IC ICM C07C013-20

ICS B01J023-72; B01J031-04; C07C002-46

ICA C07B061-00

CC 24-5 (Alicyclic Compounds)

ST alkenylcyclohexene prepn intermediate **styrene**
ethylbenzene; copper catalyst dimerization conjugated diene;
cyclization diene catalyst arom carboxylate

IT 100-41-4P, Ethylbenzene, preparation **100-42-5P**,

Styrene, preparation

(prepn. of alkenylcyclohexenes as intermediates for **styrene** and ethylbenzene from conjugated dienes)

L25 ANSWER 5 OF 31 HCA COPYRIGHT 2002 ACS

109:38427 Stabilization of **bromostyrenes** by treatment with polymerization inhibitors. Daren, Stephen L. J.; Vofsi, David; Peled, Michael (Yeda Research and Development Ltd., Israel). Brit. UK Pat. Appl. GB 2193960 A1 19880224, 3 pp. (English). CODEN: BAXXDU. APPLICATION: GB 87-017301 19870722. PRIORITY: IL 1986-79498 19860723.

AB Storage-stable **bromostyrene monomer** mixts. are obtained by heating the mixts. with excess free radical polymn. inhibitors (substituted benzenes contg. 1-3 OH groups, 1-3 alkyl groups, and 0-1 alkoxy groups), **distg.** the inhibitor-contg. mixt., and adding .ltoreq.150 ppm addnl. inhibitor. A 500 g mixt. of 70:30 mono- and **dibromostyrene** was washed with 1% NH₃ soln. and with H₂O, treated with 800 ppm tert-Bu catechol (I) heated at 65.degree. for 48 h, extd. with aq. NaOH soln., **distd.** in vacuo, dried over silica gel and treated with 150 ppm I to give a **monomer** mixt. showing good storage stability (no polymn. at 75.degree. over 72 h).

IC ICM C07C025-28

CC 35-3 (Chemistry of Synthetic High Polymers)

ST polymn inhibitor **bromostyrene butylcatechol**; storage stability **bromostyrene butylcatechol**

IT Phenols, uses and miscellaneous
(alkoxy, polymn. inhibitors, for **bromostyrenes**)

IT Polymerization inhibitors
(radical, polyhydroxybenzene derivs., for **bromostyrenes**)

IT 1335-06-4 31780-26-4, **Dibromostyrene**
(polymn. inhibitors for, polyhydroxybenzene derivs. as)

IT 27213-78-1, tert-**Butylcatechol**
(polymn. inhibitors, for **bromostyrenes**)

L25 ANSWER 6 OF 31 HCA COPYRIGHT 2002 ACS

102:132649 Inhibiting polymerization of **vinyl aromatic monomers**. Miller, Richard F.; Nicholson, Michael P. (Atlantic Richfield Co., USA). U.S. US 4487981 A 19841211, 6 pp. (English). CODEN: USXXAM. APPLICATION: US 1983-530289 19830908.

AB The polymn. of **arom. vinyl monomers** is inhibited by a stabilizer compn. comprising (a) .gtoreq.1 member selected from N,N'-dimeric, halo-substituted, and (halo)alkyl-substituted phenothiazines and (b) .gtoreq.1 mono- or di-(tertiary alkyl)dihydroxybenzene compd. selected from tertiary alkylcatechols, tertiary alkylhydroquinone, and mixt. of these. Thus, **distd. styrene** (I) [100-42-5] was mixed with 50% aq. NaOH to give 17 mg NaOH/1000 g I (10 ppm Na+), and 100 g of this mixt. was added to a flask with 200 ppm Bz2O2 and 50 ppm of a 50:50 mixt. of tert-**butylcatechol** (II) [27213-78-1] and 10,10'-diphenothiazine (III) [79430-78-7].

This flask was purged with N₂, and the reaction mixt. was heated for 2 h at 90.degree.. The amt. of **polystyrene** formed was 0.005%, compared with 10.30% in the absence of any inhibitor, 2.02% in the presence of 500 ppm II only, and 0.28% in the presence of 500 ppm III only.

IC ICM C07C007-13
 NCL 585004000
 CC 35-3 (Chemistry of Synthetic High Polymers)
 ST **styrene** polymn inhibitor; catechol butyl polymn inhibitor; hydroquinone alkyl polymn inhibitor; phenothiazine dimer polymn inhibitor
 IT Polymerization inhibitors
 (diphenothiazine mixts. with tert-**butylcatechols** and -hydroquinones, for **styrene**)
 IT 100-42-5, uses and miscellaneous
 (polymn. inhibitors for, phenothiazine mixts. with tert-**butylcatechols** and- hydroquinones as)
 IT 1322-72-1 1948-33-0 25377-22-4 27213-78-1
 (polymn. inhibitors, contg. diphenothiazine, for **styrene**)
 IT 79430-78-7
 (polymn. inhibitors, contg. tert-**butylcatechols** and -hydroquinones, for **styrene**)

L25 ANSWER 7 OF 31 HCA COPYRIGHT 2002 ACS
 101:46315 Radiation resists and manufacture. (Mitsubishi Electric Corp., Japan). Jpn. Kokai Tokkyo Koho JP 59034532 A2 19840224 Showa, 6 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1982-144334 19820820.
 GI

CH₂CH

OR I

AB Photoresist material contains an essential constituent, which is a polymer having a repeating unit I (R = Me, CH₂CH:CHMe, CH₂CH:Me, CHMeCH:CHMe). Its preparative method consists of polyimg. **monomers** including 4-vinylphenyl crotyl ether (II) in the presence of cumyl cesium. The material and the method provide high sensitivity to radiation and also high resolu. of the obtained pattern. Thus, the **monomer** for prepn. of the polymer was synthesized as in the following manner. Crotyl chloride 93.4. was added dropwise to a stirred mixt. of p-acetylphenol 140.4, K₂CO₃ 16.5, KI 16.5 g and EtOH 250 mL and refluxed with further addn. of

EtOH 250 mL. Ether extn. of the evapd. residue gave 4-acetylphenyl crotyl ether in 90% yield. The product was reduced at C=O by refluxing with NaBPh₄ and **distd.** in vacuum, and 75g of the obtained 4-(.alpha.-hydroxyethylphenyl) crotyl ether was ground with K H sulfate 0.35 g and tert-**butylcatechol** 0.1 g. Heating at 190.degree. at 2 mm Hg to carry out dehydration gave II with 50% yield. The obtained **monomer** was purified in 3 steps using CaH₂, benzophenone-Na, and combined Ph₂MeLi/LiBr, resp., all in vacuum. The solvent for polymn., THF, was also purified using CaH₂, Na metal, then using anthracene and Na metal, and finally **distd.** in the presence of .alpha.-**methylstyrene** tetramer disodium salt. Polymn. was carried out in vacuum at -78.degree. for 3 h, with cumyl cesium as catalyst. Obtained polymer was dissolved in Et Cellosolve acetate and spin-coated on Si wafer, and was irradiated with an electron beam. Development in EtCOMe/EtOH (7:1) gave a fine pattern. The radiation sensitivity was 33 times greater than that of **polystyrene**, and the pattern was resistant to dry-etching.

IC G03C001-71; G03C005-00

ICA C08F012-22

CC 74-5 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)

IT 61493-82-1P 90906-98-2P
(formation and reaction of, in prepn. of **monomer** for electron beam resist polymer prepn.)

IT 99-93-4 591-97-9 27213-78-1
(reaction of, in prepn. of **monomer** for electron beam resist polymer prepn.)

L25 ANSWER 8 OF 31 HCA COPYRIGHT 2002 ACS

99:88715 Basic **monomers**. (Asahi Chemical Industry Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho JP 58035148 A2 19830301 Showa, 8 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1981-134309 19810828.

AB **Alkylaminoethylstyrene** compds. [CH₂:CHC₆H₄CH₂CH₂NRR₁ (I); R, R₁ = H, Me, Et, iso-Pr, CH₂CH₂NH₂, cyclohexyl] were prepd. by reaction of alkylamines with divinylbenzene (II) of 10-90 % purity contg. EtC₆H₄CH:CH₂ (III) in inert org. solvent in the presence of alkylaminolithium with 20-80% conversion of II. The remaining crude II soln. was optionally concd. by **distn.** and treated with CuCl to give a complex, which was decompd. and reused as a starting material. Thus, 25.6 g 15 % BuLi in hexane was added dropwise to 35 g iso-PrNH₂ in PhMe with stirring. A mixt. (116 g) of II 56, III 41, and Et₂C₆H₄ 3% was added and the mixt. was stirred 1 h at 50.degree.; conversion of II reached 55%. Addnl., MeOH was added and the mixt. was extd. with 0.5 N HCl to give a mixt. of I (R = H, R₁ = Pr-iso) [80032-56-0] 88, (iso-PrNHCH₂CH₂)₂C₆H₄ 5, and iso-PrNHCH₂CH₂C₆H₄Et 7%, which was **distd.** with 0.1 g tert-**butylcatechol** to give 46 g I (R = H, R₁ = iso-Pr). The org. layer contg. 38% II was concd. by **distn.** and similar reaction with cyclohexylamine gave I (R = H, R₁ = cyclohexyl) [82986-66-1] of 86% purity with 40% conversion of II. Similarly prepd. were I (R = R₁ = Et) [74952-73-1], I (R = R₁ = Me)

[59480-62-5], and I (R = Me, R1 = CH₂CH₂NH₂) [86812-16-0] were prepd.

IC C07C087-452; C07C085-18
CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 25
ST **aminoethylstyrene** prepn divinylbenzene amination

L25 ANSWER 9 OF 31 HCA COPYRIGHT 2002 ACS

97:72962 **Styrene** from pyrolysis gasoline. Lipkovics, Robert Tiberiu; Mihailescu, Maria; Iordache, Irina; Antonescu, Ionel; Georgescu, Mircea; Pop, Grigore (Combinatul Petrochimic, Pitesti, Rom.). Rom. RO 70986 B 19810202, 8 pp. (Romanian). CODEN: RUXXA3. APPLICATION: RO 1977-90940 19770706.

AB Recovery of **styrene** [100-42-5] from pyrolysis gasoline was developed. Thus, pyrolysis gasoline contg. 4.84 wt.% **styrene** was fed to a column with 38 trays to remove C5 fraction as overhead, and the residue was fed to the next column with 45 trays where a C₆H₆-PhMe fraction was removed as overhead and the residue was fed to the next vacuum column with 38 trays to recover **styrene** conc. as overhead. p-tert-**Butylcatechol** was added to the reflux of the last 2 columns as a polymn. inhibitor. The **styrene** conc. was hydrogenated over a Pd/Al₂O₃ catalyst at space velocity 5 h⁻¹, 30.degree., and 10 atm, oxidized with a soln. of 75% HNO₃ and 1% KMnO₄ soln., and neutralized with NaOH soln. The conc. after neutralization was fed to an extractive **distn.** column with 120 trays where N-methylpyrrolidone was used as a solvent. Xylene conc. was obtained as the overhead and **styrene**-satd. solvent as the residue which was fed to a desorption column with 55 trays to free **styrene** and recover solvent. **Styrene** was washed with H₂O in a column to remove traces of solvent and then fed to a **distn.** column with Raschig packing where p-tert-**butylcatechol** was fed as a polymn. inhibitor. Polymer-grade **styrene** was obtained as overhead. The recovery of **styrene** was 88%.

IC C07C015-10
CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 51
ST **styrene** recovery pyrolysis gasoline
IT Gasoline
(pyrolysis, **styrene** from)
IT 100-42-5P, preparation
(recovery of, from pyrolysis gasoline)

L25 ANSWER 10 OF 31 HCA COPYRIGHT 2002 ACS

84:122554 Sulfonic acid esters from free sulfonic acids. Schroeck, Calvin W. (Lubrizol Corp., USA). U.S. US 3937721 19760210, 5 pp. (English). CODEN: USXXAM. APPLICATION: US 1974-468359 19740509.
AB 2-Acrylamido-2-methylpropanesulfonic acid (I) [15214-89-8] is esterified with Et₃PO₄ [78-40-0] or Me₂SO₄ [77-78-1] and the Me ester (II) [54545-52-7] is copolymd. with vinyl or acrylic **monomers** to give dyeable polymers. The esterification

avoided the disadvantages assocd. with using the acid chloride or a direct esterification reagent such as diazomethane. Thus, to 63 g Me₂SO₄ and 37 g DMF (kept 3 hr at 60-80.degree.) are added 700 ml C₆H₆ and I 52, p-MeOC₆H₄OH 0.3, tert-**butylcatechol** 0.3, and 2,6-di-tert-butylcresol 0.3 g, and the mixt. is refluxed 24 hr, the C₆H₆ **distd.**, and refluxing continued 24 hr at 78-80.degree. to give II. Acrylonitrile-I polymer [54640-82-3], **styrene**-I polymer [54545-54-9], and isodecyl acrylate-I polymer [54667-13-9] were prepd.

IC C07C

NCL 260456000A

CC 35-2 (Synthetic High Polymers)

Section cross-reference(s): 23

IT 54545-52-7P

(prepn. and copolymn. of, with acrylic **monomers**)

L25 ANSWER 11 OF 31 HCA COPYRIGHT 2002 ACS

83:59751 Separating and purifying **styrene**. Tatsumi, Masanori; Abe, Kuro (Toray Industries, Inc.). Japan. JP 49016408 B4 19740422 Showa, 3 pp. (Japanese). CODEN: JAXXAD. APPLICATION: JP 1969-83223 19691020.

AB **Styrene** was sepd. by extractive **distn.** of cracked oil in the presence of a Diels-Alder reactant. Thus, a vacuum **distd.** cracked oil, comprising ethylbenzene 7, p-xylene 9, m-xylene 22, o-xylene 17, **styrene** 39, propylbenzene 2, methylethylbenzene 3, and trimethylbenzene 1%, was extractively **distd.** 4 hr by using AcNMe solvent contg. 0.5% maleic anhydride and 50 ppm p-tert-**butylcatechol** as polymn. inhibitor to give a colorless compn. contg. 80% **styrene**.

IC C07C

CC 35-2 (Synthetic High Polymers)

Section cross-reference(s): 51

ST **styrene** sepn cracked petroleum; Diels Alder

styrene sepn; maleic anhydride **styrene** sepn

IT Diels-Alder reaction

(in **styrene** sepn., from cracked naphtha **distillate**)

IT Naphtha

(**styrene** sepn. from **distillate** of cracked, by extn. **distn.** in presence of Diels-Alder reactants)

IT 108-31-6, uses and miscellaneous

(in **styrene** sepn., from cracked naphtha **distillate**)

IT 100-42-5P, preparation

(sepn. of, from cracked naphtha **distillate**, by extn. **distn.** in presence of Diels-Alder reactants)

L25 ANSWER 12 OF 31 HCA COPYRIGHT 2002 ACS

83:11142 Separating **styrene** from naphtha-cracked residual oil.

Abe, Hisao; Tatsuno, Masanori (Toray Industries, Inc., Japan).

Japan. JP 50001009 B4 19750114 Showa, 4 pp. (Japanese). CODEN:

- JAXXAD. APPLICATION: JP 1970-72052 19700819.
- AB **Styrene** [100-42-5] was recovered from C8 arom. hydrocarbon fractions (obtained from crude naphtha-cracked residual oil) by extractive **distn.** with a polar org. solvent contg. Na nitrite (I) [7632-00-0] polymn. inhibitor. In an example, a mixt. contg. **styrene** 63, xylene 25, propylbenzene 2, and ethylmethylbenzene 2% was extractively **distd.** with MeCONMe2 contg. 200 ppm I. Loss of **styrene** due to thermal polymn. was 1%; use of tert-butylcatechol in place of I gave 8% **styrene** loss.
- IC C07C
- CC 35-2 (Synthetic High Polymers)
Section cross-reference(s): 25
- ST **styrene**; polymn inhibitor sodium nitrite; extractive **distn styrene** mixt
- IT Polymerization inhibitors
(sodium nitrite as, for **styrene** during extractive **distn.** from hydrocarbon mixts.)
- IT 100-42-5P, preparation
(extractive **distn.** of, from hydrocarbon mixts., polymn. inhibitors for)
- IT 7632-00-0
(polymn. inhibitor, for **styrene** during extractive **distn.**)
- mlg*

82:97805 Separation of C9-10 aromatic hydrocarbons having unsaturated side chain by extractive **distillation**. Wada, Toru (Kuraray Co., Ltd.). Jpn. Kokai Tokkyo Koho JP 49086330 19740819 Showa, 5 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1973-2185 19721225.

AB C9-10 arom. hydrocarbons having unsatd. side chain are sepd. from a mainly arom. hydrocarbon mixt. by extractive **distn.** with N,N-dialkylbenzamides, N,N-dialkylpropionamides, N,N-dialkylbutyramides, tetramethylene sulfoxide, PhCN, alkylbenzonitriles, (NCCH₂CH₂)₂O, PhNO₂, alkylnitrobenzenes, (MeO)₃PO, (Me₂N)₃PO, sulfolane, and (or) PhOAc. Thus, a mixt. of 10% mesitylene, 55% pseudocumene, and 35% vinyltoluene (65:35 m- and p-isomers) was subjected to extractive **distn.** in a series of 2 bubble-cap towers at 30-50 mm with BzNMe₂ contg. 50 ppm tert-butylcatechol to give vinyltoluene of 99.9% purity, vs. 81% for the control (no BzNMe₂). .alpha.-**Methylstyrene** or indene were similarly sepd.

NCL 16C1

CC 25-2 (Noncondensed Aromatic Compounds)

ST vinyltoluene purifn; toluene vinyl extractive **distn**; **styrene** methyl purifn; indene purifn benzamide

IT 611-74-5P

(extractive **distn.** of benzene with unsatd. side chains by)

IT 95-13-6P **98-83-9P**, preparation 100-80-1P 622-97-9P (purifn. of, from arom. hydrocarbons, by extractive **distn** .)

L25 ANSWER 15 OF 31 HCA COPYRIGHT 2002 ACS

82:97804 Separation of C9-10 aromatic hydrocarbons having unsaturated side chain by extractive **distillation**. Wada, Toru (Kuraray Co., Ltd.). Jpn. Kokai Tokkyo Koho JP 49086331 19740819 Showa, 5 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1973-2186 19721225.

AB C9-10 arom. hydrocarbons having unsatd. side chain are sepd. from a mainly arom. hydrocarbon mixt. by extractive **distn.** with N,N-dialkylacetamides, N-alkylpyrrolidones, N-alkylcaprolactams, dialkyl sulfoxides, .gamma.-butyrolactone, .gamma.-valerolactone, .epsilon.-caprolactone, and (or) alkylene carbonates. Thus, a mixt. of 10% mesitylene, 55% pseudocumene, and 36% vinyltoluene (65:35 m- and p-isomers) was subjected to extractive **distn.** in a series of 2 bubble-cap towers at 30-50 mm with N-methylpyrrolidone contg. 50 ppm tert-butylcatechol to give vinyltoluene of 99.9% purity, vs. 81% for the control (no solvent). .alpha.-**Methylstyrene** or indene were similarly sepd.

NCL 16C1

CC 25-2 (Noncondensed Aromatic Compounds)

ST vinyltoluene purifn; toluene vinyl extractive **distn**; **styrene** methyl purifn; indene purifn pyrrolidone

IT 872-50-4P

(extractive **distn.** of benzene with unsatd. side chains by)

IT 95-13-6P **98-83-9P**, preparation 100-80-1P 622-97-9P
(purifn. of, in presence of arom. hydrocarbons)
IT 27213-78-1
(sepn. of benzenes with unsatd. side chains by extractive
distn. in presence of)

L25 ANSWER 16 OF 31 HCA COPYRIGHT 2002 ACS
81:78467 **Styrene**. Morimoto, Hiroshi (Toray Industries, Inc.).
Japan. Kokai JP 49031625 19740322 Showa, 4 pp. (Japanese).
CODEN: JKXXAF. APPLICATION: JP 1972-74110 19720726.

AB **Styrene** (I) [100-42-5] was manufd. from
hydrocarbon oil cracking products by extractive **distn.**
followed by alkali treatment. A cracking oil contg. 6% I was
distd. to give a C8 run contg. 39% I which was extractively
distd. with DMF and washed with water to give crude I (purity
99.7%). The crude I (370 ml) was shaken with 37 ml 10% aq. NaOH,
washed with water, and rectified with 0.1 wt. % tert-
butylcatechol to give a colorless **monomeric**
product.

NCL 16C1

CC 35-2 (Synthetic High Polymers)

ST cracking oil **styrene** manuf; hydrocarbon oil
styrene manuf

IT Hydrocarbon oils

(cracking products, **styrene** manuf. from, by extractive
distn.)

IT 100-42-5P, preparation

(from hydrocarbon oil cracking products, by extractive
distn.)

L25 ANSWER 17 OF 31 HCA COPYRIGHT 2002 ACS

78:30480 Rendering **styrene** colorless by artificial light
irradiation. Newsom, Raymond A.; McLeod, Richard K.; Ruland, Norman
L. (Monsanto Co.). U.S. US 3702811 19721114, 2 pp. (English).
CODEN: USXXAM. APPLICATION: US 1971-164929 19710721.

AB Color developed in **styrene** [100-42-5] on storage
is removed without **distn.** by treatment with 3000-7000
lang. light. Thus, **styrene** contg. 10-15 ppm tert-
butylcatechol when recirculated with exposure to a 10,500
lumen Hg arc lamp has APHA color 6 after 7 days, compared with 23 in
the absence of light exposure.

IC B01D; C07C

NCL 204158000R

CC 35-2 (Synthetic High Polymers)

ST light decolorization **styrene**; color stability
styrene

IT Light, chemical and physical effects
(decolorization by, of **styrene**)

IT Bleaching

(photochem., of **styrene**)

IT 100-42-5P, preparation

(decolorization of, by light)

L25 ANSWER 18 OF 31 HCA COPYRIGHT 2002 ACS

77:115440 Curable unsaturated poly(ester-amides). Jain, Devendra; Goodman, Isaac (Imperial Chemical Industries Ltd.). Brit. GB 1281752 19720712, 8 pp. (English). CODEN: BRXXAA. APPLICATION: GB 1969-28457 19690605.

AB The title prepolymers are prepd. from .geq.1 diol with .geq.1 dicarboxylic acid; .geq.1 of the components contain crosslinkable satn. and part of the diol component contains .geq.1 amide group in the chain of atoms connecting the 2 OH groups. Thus maleic anhydride [108-31-6] 245, propylene glycol [57-55-6] 130.4, and N,N'-bis(6-hydroxycaproyl)hexamethylenediamine [36011-12-8] 101 parts were heated with stirring under N to 150.deg. during 1 hr and held for 4 hr. Water of reaction was **distilled** and 0.025 part 2,5-di-tert-butylhydroquinone was added and the temp. raised to 180.deg.. The pressure was reduced to 15 cm Hg absolute and the reaction continued to the desired acid value. A 1:2 mixt. (0.125 part) of hydroquinone and p-tert-**butylcatechol** was added and the resin cooled under N; the viscous liquid had acid value 56. The poly(ester amide) resin was mixed with stabilized **styrene** [100-42-5] or 2-hydroxyethyl methacrylate [868-77-9] and cured with a peroxide catalyst system. The solvent resistance index was detd. by immersing samples of the cast sheets in acetone for 24 hr at 25.deg.; the samples were only slightly effective as compared with a control (a general purpose resin based on a conventional mixt. of **styrene** and unsatd. polyester) which was almost disintegrated.

IC C08G

CC 36-6 (Plastics Manufacture and Processing)

ST curing polyester amide compns; polyamide polyester compn; prepolymer polyester amide; solvent resistance unsatd polyester; vinyl polyester amide copolymers; **styrene** polyester amide copolymer

IT Polyesters, uses and miscellaneous
(amide-modified, solvent-resistant molding compns. from **styrene**-crosslinked)

IT Crosslinking
(of unsatd. polyesteramides, with **styrene**)

IT Polyamides, uses and miscellaneous
(polyester-modified, solvent-resistant molding compns. from **styrene**-crosslinked)

IT 100-42-5, uses and miscellaneous 868-77-9
(crosslinking agents, for solvent-resistant polyesteramides)

IT 38807-60-2 38807-61-3 38807-62-4 38891-62-2
(crosslinking of solvent-resistant, with **styrene**)

L25 ANSWER 19 OF 31 HCA COPYRIGHT 2002 ACS

76:86739 Effect of addition of cardanol on peroxide curing of polyester resins. Jain, R. K.; Asthana, K. K. (Cent. Build. Res. Inst., Roorkee, India). Pop. Plast., 16(11), 26-9 (English) 1971. CODEN: POPPAB.

AB The effect of the addn. of cardanol, prepd. by the **distn.**

of cashew nut shell liq., on the curing of polyester resin is reported. Thus to phthalic anhydride-maleic anhydride-fumaric acid-propylene glycol polyester [34012-52-7] contg. hydroquinone-tert-butylcatechol inhibitor, MeCOEt peroxide catalyst and Co accelerator in 30% **styrene** [100-42-5] was added 0-10% cardanol and 1% Bz2O2 and the mixt. cured at 82.deg.; cardanol inhibits the curing so that gel time and cure time are increased and the peak exotherm decreased. At .geq.5% cardanol no exotherm is recorded and >90 min. are required to gel. Flexural strength of polyester resin sheets cured at 70.deg. with cardanol showed higher values (e.g., 1% cardanol gave flexural strength 520 compared with 403 kg/cm2 for the control). The probable crosslinking provided by cardanol was confirmed by adding addnl. **styrene** [100-42-5] to the resin in place of cardanol, and the flexural strength increased .leq.5% addnl. **styrene** and then decreased. The resulting net structures may be polyester-**styrene**-cardanol copolymers and are useful as extended pot life resins, low exotherm resins, and potting resins.

CC 37 (Plastics Fabrication and Uses)

IT 34012-52-7

(crosslinking of **styrene**-contg. compns., cardanol effect on)

L25 ANSWER 20 OF 31 HCA COPYRIGHT 2002 ACS

76:59178 **Distillation** of **styrene** containing a polymerization inhibitor and contact of the bottoms stream with an alcohol. Jones, Edwin K. (Universal Oil Products Co.). U.S. US 3629076 19711221, 5 pp. (English). CODEN: USXXAM. APPLICATION: US 19700908.

AB The bottoms product of a **styrene distn.** column contg. **polystyrene**, S, tert-butylcatechol, undistd. **styrene**, and, optionally, cut-back oil was treated with alc. to ppt. **polystyrene** and part of the S. The remaining liq., including the remaining portion of the S was recycled back into the system.

IC B01D

NCL 203009000

CC 25 (Noncondensed Aromatic Compounds)

Section cross-reference(s): 68

ST sulfur recovery **styrene distn**

IT 100-42-5P, preparation

(**polystyrene** and sulfur removal from **distn.** residue)

IT 67-56-1, uses and miscellaneous

(pptn. of **polystyrene** and sulfur by)

IT 7704-34-9P, preparation 9003-53-6P

(recovery of, from **styrene distn.** residue)

L25 ANSWER 21 OF 31 HCA COPYRIGHT 2002 ACS

75:140458 Recovery of **styrene** and xylenes from naphtha cracking oils. Abe, Hisabo; Tatsumi, Masanori (Toray Industries,

Inc.). Ger. Offen. DE 2006863 19710909, 32 pp. (German). CODEN: GWXXRY. APPLICATION: DE 1970-2006863 19700214.

AB **Styrene** and xylenes were recovered from oils from cracking of naphtha, for the manuf. of ethylene, by extractive **distn** . together with a solvent. Thus, a cracking oil fraction of b.p. 130-50.degree. and 7.5% **styrene** content was **distd** . with addn. of AcNMe₂ (contg. 300 ppm **tertbutylcatechol**) at 60.degree./70 mm and reflux ratio 12 in a first column contg. 50 plates to give a mixt. contg. PhEt 21, p-xylene 18, m-xylene 36, and o-xylene 25%. The residue from the first **distn**. was **distd**. together with AcNMe₂ in a 2nd column contg. 60 plates at 45.degree./20 mm and reflux ratio 15 to give 86% **styrene** of 99.2% purity. Similarly used were 14 other solvents, e.g. Me₂SO, (Me₂N)₂CO, propylene carbonate, PhOH, or PhNH₂.

82:156996 Separation and purification of **styrene**. Morimoto,
Hiroshi; ~~Tatsumi~~, Masanori (Toray Industries, Inc., Japan). Japan.
JP 50002498 B4 19750127 Showa, 4 pp. (Japanese). CODEN: JAXXAD.

AB APPLICATION: JP 1970-12480 19700214.
A C8 arom. hydrocarbon fraction, obtained by **dist.** of
cracked oil, was heated at 60-160.degree. for 5 min to 3 hr in the
presence of a polymn. inhibitor, treated with a Diels-Alder reaction
reagent such as maleic anhydride (I) [108-31-6] at 50-100.degree.
for 15-30 min, and **distd.** to give colorless
styrene (II) [100-42-5] without loss by polymn.
Thus, a fraction contg. 39 wt.% II was heated 1 hr at 120.degree. in
the presence of tert-**butylcatechol** [27213-78-1] (0.05 wt.%
based on II), then 2 hr at 70.degree. in the presence of I (0.5 wt.%
based on II), and **distd.** to give II suitable for
polystyrene manuf.

IC C07C
CC 35-2 (Synthetic High Polymers)
ST **styrene** purifn **distn**; maleic anhydride purifn
styrene; catechol purifn **styrene**
IT 108-31-6, uses and miscellaneous 27213-78-1
(in purifn. of **styrene** by **distn.**)
IT 100-42-5P, preparation
(purifn. of, by **distn.** in presence of tert-
butylcatechol and maleic anhydride)

polyester casting was made by stirring 1.1 g. of 50% (BZO)₂ into 35 g. of the resin and heating to 83.degree. until max. exotherm had been observed, and curing at 130.degree. for 21 hrs.

NCL 260869000

CC 48 (Plastics Technology)

IT Esters, poly-
(halogen-contg., and fire-resistant resins with **styrene**
)

L25 ANSWER 23 OF 31 HCA COPYRIGHT 2002 ACS

64:68550 Original Reference No. 64:12870g-h,12871a-c Polymerizable alkenylbenzyl polyglycol ethers. Stowe, Stephen C. (Dow Chemical Co.). US 3190925 19650622, 4 pp. (Unavailable). APPLICATION: US 19590810.

AB Alkenylbenzyl polyglycol ether **monomers** are used to prep. polymers that are useful as additives for synthetic textile fibers, such as polyacrylonitrile fibers, as antistatic agents or as humectant dye receptors, or as stabilizers. Thus, 100 g. NaOH was stirred with 300 g. of the mono-Me ether of diethylene glycol to give a partial soln. About 252 cc. 4-vinylbenzyl chloride contg. 0.01 wt. % tert-**butylcatechol** was slowly added. With ice water cooling the temp. rose to 90.degree. but was maintained at 50-60.degree. for most of the reaction. The NaCl was filtered off and the filtrate **distd.** to give about 50% of the initial charge b0.3 144-50.degree., d₂₅ 1.03, equiv. wt. by bromide-bromate titrn. 120. A **monomer** of mol. wt. 316, similarly prepd., was copolymerized with acrylonitrile to give copolymers which had good fiber-forming properties, were humectant and relatively hydrophilic in nature as compared with polyacrylonitrile, and were readily dyeable with a wide variety of dyes. A mixt. of 31.5 g. poly(N-vinyl-2-pyrrolidinone) Fikentscher K-value .apprx.45, 7.2 g. 1-(2-methoxyethoxy)-2-(4-vinylbenzyloxy)ethane, 6.3 g. Na **styrene-sulfonate**, 0.5 g. K₂S₂O₈, and 181.8 g. H₂O was brought to pH 6 by acidification with HCl. The mixt. was stirred at about 60.degree. for 19 hrs. with N being passed through slowly. The graft copolymer contained 14% polymerized polyglycol ether units, 11% polymerized Na **styrenesulfonate** units, and 75% poly(N-vinyl-2-pyrrolidinone). Polyacrylonitrile fibers contg. 10% of the graft copolymer dyed well to deep and level shades with Calcodur Pink 2BL and Sevron Brilliant Red 4G. The elec. cond. was superior to ordinary polyacrylonitrile and only slightly poorer than cotton. The phys. properties were equal to those of unmodified polyacrylonitrile fibers. An oriented polyacrylonitrile aquagel fiber contg. 1 part polymer hydrated with 2 parts H₂O was soaked for 15 min. at 70.degree. in a 40% aq. soln. of polyglycol 4-vinylbenzyl ether obtained from a polyethylene glycol having a av. mol. wt. of 600. The wet fiber, after being drained of excess impregnating soln., was sealed in a polyethylene bag and irradiated with high-energy x-irradiation. The irradiated yarn was dyed with Amacel Scarlet 35 to a deep and level coloration. Unmodified yarn could be dyed to only a very slight degree with the same dye.

NCL 260611000

CC 47 (Textiles)

L25 ANSWER 24 OF 31 HCA COPYRIGHT 2002 ACS

62:59353 Original Reference No. 62:10540g-h,10541a Polymerization inhibitors. Joo, Louis A. (Pure Oil Co.). US 3167596 19650126, 3 pp. (Unavailable). APPLICATION: US 19611026.

AB Dialkenyl amines derived from aromatic heterocyclic amines are effective polymerization retarders at room temp. and improve the storage life of **monomers**, e.g. diallyl maleate, **styrene**, butadiene, and acrylonitrile. Thus, 45 g. Na was heated above its m.p. in 500 g. xylene with stirring. The dispersion was cooled to 50.degree., 300 ml. pyridine (I) was added, the mixt. heated 4-6 hrs. at 50.degree., and 2 moles 3-chloropropene was then added dropwise with stirring. The mixt. was stirred for an addnl. 4 hrs. Unreacted I was **distd.**, and the residue was acidified with HCl. The aq. phase was sepd. and neutralized, pptg. the product dipropenyltetrahydrodipyridyl. Similarly prepd. was diallyltetrahydrodipyridyl (II); 0.12% II was added to **styrene** contg. 0.26% Me Et ketone peroxide. After 13 days, the viscosity was 32 poises, compared with 40 for a control contg. no II, and 27 for a control contg. p-tert-**butylcatechol** (III). A sample of this accelerated **styrene** contg. 2% II had a viscosity of 0.5 poises after 13 days. A gelation test showed that II does not retard polymerization at 90.degree. as much as does III.

NCL 260666500

CC 45 (Synthetic High Polymers)

L25 ANSWER 25 OF 31 HCA COPYRIGHT 2002 ACS

62:29789 Original Reference No. 62:5297f-h,5298a-b **Vinylidene aromatic phosphorus monomers**. Abramo, John G.;

Garner, Albert Y.; Chapin, Earl C. (Monsanto Co.). US 3161667 19641215, 5 pp. (Unavailable). APPLICATION: US 19600104.

GI For diagram(s), see printed CA Issue.

AB The title compds. were prepd. by contacting a .beta.-haloalkyl halomethyl aromatic compd. with an organophosphorus compd. at 50-200.degree. and dehydrohalogenating the product in the presence of an alkali metal base. E.g., 75 g. p-(.beta.-chloroethyl)benzyl chloride and 66 g. (EtO)₃P were charged to a stirred reactor and held at 85-90.degree. 20 hrs. The mixt. was **distd.** in vacuo, transferred to a 2nd stirred reactor, and to it was added 0.1 g. tert-**butylcatechol** and a soln. of 23 g. KOH in 500 ml. EtOH. The mixt. was refluxed 6 hrs., poured into H₂O, extd. with C₆H₆, **distd.** to remove H₂O and C₆H₆ and then **distd.** in vacuo to yield di-Et p-vinylbenzyl phosphonate, b0.2 120.degree.. Similarly prepd. were di-Ph m-vinylbenzyl phosphonate (I), Et p-isopropenylbenzyl methylphosphinate (II), 1-vinyl-4- Et phenylphosphinatomethyl-naphthalene (III), p-vinylbenzyl diphenylphosphine oxide, p-vinylbenzyl diisopropylphosphine oxide, Et p-(.beta.-chloroisopropyl)benzyl methylphosphinate, 1-(.beta.-chloroethyl)-4-(Et phenylphosphinatomethyl)naphthalene, p-(.beta.-chloroethyl)benzyl diphenylphosphine oxide. In an example

of polymerization of these **monomers**, 15 g. I and 0.1 g. di-tert-Bu peroxide were charged to a reaction tube, placed under an inert atm. and held at 80.degree. 15 hrs. A hard, transparent, amorphous polymer was produced. The **monomers** are useful as flameproofing agents or for producing flame-resistant polymers.

NCL 260461000

CC 39 (Organometallic and Organometalloidal Compounds)

L25 ANSWER 26 OF 31 HCA COPYRIGHT 2002 ACS

61:82764 Original Reference No. 61:14363h,14364a-c Removal of anions from aqueous solution. Kressman, Theodore R. E.; Millar, John R. (Permutit Co. Ltd.). US 3147214 19640901, 6 pp. (Unavailable). PRIORITY: GB 19580709.

AB Both org. impurities and inorg. anions are removed from an aq. liquid by treating it with a particulate anion- exchange resin contg. strongly basic groups and produced by copolymerizing a **monomer** having one polymerizable double bond, and at least 25% of a cross-linking agent having two polymerizable double bonds, in a soln. in an org. liquid which is a solvent for the **monomer** mixt. but is not a solvent for the copolymer at room temp., the solvent constituting from 30% to 80% of the total mixt. The anion- exchange resin contains pores having a mean pore diam. of .gtoreq.100 A., with .gtoreq.10% of it total pore vol. in the form of pores >350 A. in width. Thus, 10 g. azobisisobutyronitrile was dissolved in a mixt. of 150 cc. **styrene**, 250 cc. of a com. divinylbenzene soln. (contg. 50% divinylbenzene and 50% **ethylstyrene**), and 800 cc. of toluene. The soln. was stirred with water contg. a suspension stabilizer (0.1% poly(vinyl alc.)) so as to form globules of particle size about 14 to 52 mesh. The whole was heated to about 75.degree. with continuous stirring for 18-24 hrs., after which time polymerization was substantially complete and the globules had become converted to solid spheres. A soln. of 1 g. tert-**butylcatechol** in 100 cc. toluene was then added and the stirring continued for an addnl. 1 hr. Finally, the toluene was removed by **distn.** and the toluene-free polymer beads filtered off from the water and dried at 100.degree.. The dried beads were swollen in 1.5 l. ethylene dichloride and a mixt. of 940 g. chloromethyl ether contg. 350 g. powd. anhyd. AlCl₃ was then added. The whole was warmed to 60.degree.-65.degree. for 12 hrs., then poured into an excess of water and the beads filtered off and washed with water. They were then covered with 2 l. of 25% aq. Me₃N soln. and left in the cold for 12 hrs. The resulting aminated beads were filtered off and washed with dil. HCl and then with water.

NCL 210024000

CC 24 (Water)

IT 9003-70-7, Benzene, divinyl-, polymer with **styrene**
(macroporous aminated chloromethylated, for water treatment)

L25 ANSWER 27 OF 31 HCA COPYRIGHT 2002 ACS

58:21407 Original Reference No. 58:3583d-e Copolymers of 1,1,2,3-tetrachloro-1,3-butadiene. Stewart, Clare A., Jr. (E. I. du

Pont de Nemours & Co.). US 3058960 19621016, 2 pp. (Unavailable).
APPLICATION: US 19600217.

- AB Copolymers of 1,1,2,3-tetrachlorobutadiene (I) with **styrene** (II) or chloroprene (III), having good tensile properties and high freeze-resistance, were prepd. For example, I 2.94 was treated with II 7.22 and Bz2O2 0.036 g. at 80.degree. for 1 hr. The copolymer was pptd. with MeOH, washed with H2O, and dried. Similarly, I 30 and III 171, in the presence of Cl2H25SH 0.42, rosin 6, Na2SO3 0.6, NaOH 1.1, H2O 300, and the Na salt of a condensation product of HCHO and naphthalenesulfonic acid. 0.8 g., were polymerized at 40.degree. with 2% K2S2O8 to a sp. gr. of 1.063. The reaction was stopped with phenothiazine and tert-**butylcatechol** (0.05 g. each), the excess **monomer distd.**, and the polymer pptd. with AcOH, washed with Me2CO and H2O, then milled to dryness with 1.5 g. MgCO3. Soft yellow rubber (125 g.) contg. 40.5% Cl was obtained. The copolymers were compounded as usual. I (b20 65-8%, d. 1.468, n25D 1.5240) was prepd. by dehydrohalogenation of 1,1,2,2,3,4-hexachlorobutane.
- NCL 260087500
- CC 49 (Rubber and Other Elastomers)
- IT 1,3-Butadiene, 1,1,2,3-tetrachloro-, polymers, with 2-chloro-1,3-butadiene or **styrene** (freeze-resistant tensile)

L25 ANSWER 28 OF 31 HCA COPYRIGHT 2002 ACS

56:8342 Original Reference No. 56:1617e-i,1618a-b Emulsion polymers and copolymers. Boussu, Gabriel Xavier Roger; Saint-Frison, Louis H. N.; Neuville, Louis P. F. A. (Compagnie Generale des Etablissements Michelin Raison Sociale; Robert Puiseux & Co.). DE 1102402 19581007 (Unavailable). PRIORITY: FR 19590914.

- AB High polymerization rates at low temp. in emulsion systems are achieved by carrying out the emulsion polymerization in the presence of an org. polyhalide, a reducing agent, a nitrogenous base, and a Cu catalyst. The polyhalide has the general formula C_nX_{2n+2} , where $1 < n < 3$ and X is Cl or Br, and is present in the reaction mixt. in amts. of 0.8-1.6% of the wt. of **monomer**. The Cu is added in ionic concns. of 3-150 mg./100 l. H2O in the form of a sol. salt. The reducing agent can be HCHO, HSO3 -, HPO2 --, or N2H4, and must be present in excess with respect to the polyhalide. The org. base should have a KB < 10-6 and must form no complex with Cu. Preferably a base is used which can be recovered by **distn** ., e.g. NH3, aliphatic, aromatic, or heterocyclic amines, in concns. of 0.05-2.0M. The catalyst system described enables polymerizations to be carried out at high rates and low temps. It also permits the plasticity of the end product to be predetd. The mole ratio of polyhalide/Cu affects the mol.-wt. distribution of the polymer and the rate of copolymerization. By using the catalyst system, **monomer** stabilizers need not be removed prior to polymerization. The reaction can be stopped by the addn. of a complexing agent for Cu. For example, C2Cl6 0.7 and oleic acid 3.5 were dissolved in isoprene 100 parts. A soln. of NH3 (22.degree. Be.) 100, N2H4.H2O 0.2, CuSO4.5H2O 0.00035, FeSO4.7H2O 0.002, and

tartaric acid 0.03, in water 100 parts was prepd. The two solns. were mixed in a closed vessel and stirred for 24 hrs. at 20.degree.. A 75% yield of polymer was obtained. By omitting the C_2Cl_6 no reaction took place and the velocity and yield were considerably reduced by substituting NH_3 by NaOH , or N_2H_4 by Na_2HPO_2 or by $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$. A mixt. of H_2O 200, piperidine 12, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ 0.2, NaOH 0.9, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.0003, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.0005, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 0.0002, and tartaric acid 0.005 part was placed in an autoclave which was then evacuated. Butadiene (98%) 74 parts contg. 100 p.p.m. **tert-butylcatechol** (I) was pumped in, and a soln. of phenyl-.beta.-naphthylamine 1, oleic acid 3.3, and CCl_4 1.2 dissolved in **styrene** 26 parts contg. 15 p.p.m. I was also introduced. The mixt. was stirred for 10 hrs. at 21.degree.. The polymerization was stopped by the addn. of NaCN 0.001 part. The piperidine and the residual **monomer** were recovered by blowing steam through the reaction mixt. After acid coagulation of the latex, 86 parts of benzene-sol. rubber contg. 21% **styrene** and having a Mooney plasticity of 58 was obtained. By comparison with a com. **butadienestyrene** rubber of the same elasticity modulus, measured at 250% elongation, an improved abrasion resistance (7%) and hysteresis (9%) were obtained. Detailed examples are given to show how the plasticity of the rubber depends on the Cu concn. in the mixt., and of the emulsion polymerization of **styrene** and poly(vinyl chloride).

NCL

39C

CC 47 (Plastics)

IT Copper sulfate, acidic

(catalysts in polymerization of butadiene with **styrene** and of isoprene in emulsion)IT 56-23-5, Carbon tetrachloride 7646-79-9, Cobalt chloride, CoCl_2 (catalysts, in polymerization of butadiene with **styrene** in emulsion)IT 7720-78-7, Iron sulfate, FeSO_4 (catalysts, in polymerization of butadiene with **styrene** or isoprene in emulsion)

L25 ANSWER 29 OF 31 HCA COPYRIGHT 2002 ACS

55:96613 Original Reference No. 55:18175a-e Graft copolymers of p-**isopropylstyrene** and methyl methacrylate. Matlack, J. D.; Chinai, S. N.; Guzzi, R. A.; Levi, D. W. (Picatinny Arsenal, Dover, NJ). J. Polymer Sci., 49, 533-41 (Unavailable) 1961.

AB Completely isopropylated **polystyrene** is produced by polymerization of p-**isopropylstyrene monomer**. This polymer is autoxidized in cyclohexane with lauroyl peroxide. Me methacrylate is grafted to the polymeric hydroperoxide by using a sugar-contg. recipe. Thus, cumene was converted to p-isopropylacetophenone by treating it with AcCl by using anhyd. AlCl_3 as catalyst and CCl_4 as solvent. The p-isopropylacetophenone was obtained by **distn.** by using a 20-in. Vigreux column (b.p. 68-72.degree. (0.80 mm.); $n_{25D} = 1.5211$). p-Isopropylacetophenone was converted to p-isopropylphenyl(methyl)carbinol (I) by using LiAlH_4 in ether. I was

then added to fused KHSO₄ contg. tert-butylcatechol and hydroquinone at 225-35.degree.. The resulting p-isopropylstyrene monomer was obtained by distn. by using a 20-in. Vigreux column (b.p. 45.degree. (1.3 mm.); n_D²⁴ = 1.5190). Poly(p-isopropylstyrene) was prepd. by bulk polymerization at 60.degree. by using azodiisobutyronitrile initiator. The polymeric hydroperoxide used to initiate polymerization was prepd. by autoxidn. of poly(p-isopropylstyrene). It was found that by passing O through a cyclohexane soln. of the polymer at 75.degree. and by using lauroyl peroxide (5% of polymer), the oxidn. could be accomplished without formation of colored products. Grafting was carried out at 30.degree. by using the following recipe: Me methacrylate monomer 100, H₂O 200, C₆H₆ 200, autoxidized poly(p-isopropylstyrene) 20, FeSO₄.7H₂O 0.28, Na₄P₂O₇.10H₂O 0.45, D-levulose 1.00, and SF flakes 5 parts. The per cent conversion was followed by detg. solids content on suitable aliquots. The latex was coagulated by addn. to MeOH. The polymer was pptd. from C₆H₆ with MeOH and dried under reduced pressure at room temp. Considerable quantities of poly(methyl methacrylate) were formed in the graft copolymer and partially removed by fractional pptn. from C₆H₆ by addn. of MeOH. Further purification was obtained by extn. with a 2:1 mixt. of acetone-MeOH which dissolved the poly(Me methacrylate). Evidence for grafting was obtained by light-scattering and viscosity measurements.

CC 31 (Synthetic Resins and Plastics)

L25 ANSWER 30 OF 31 HCA COPYRIGHT 2002 ACS

53:111663 Original Reference No. 53:19982g-i Neutral diesters of 2,2'-[isopropylidenebis(2,6-dichloro-p-phenyleneoxy)]diethanol. Hurd, Everett C.; Petras, John F. (United States Rubber Co.). US 2891092 19590616 (Unavailable). APPLICATION: US .

AB Ester interchange between dialkyl fumarates and certain diethanols yielded compds. which copolymerized with ethylenic monomers to give heat- and light-stable plastics. Thus, 2,2'-[isopropylidenebis(2,6-dichloro-p-phenyleneoxy)]diethanol (I) (227 g.), 216 g. di-Me fumarate, 200 ml. toluene, and 0.8 g. p-tert-butylcatechol was refluxed until all water had been removed azeotropically, 4.4 g. Mg added, and the mixt. distd . to remove MeOH-toluene azeotrope at 65-9.degree.. Reaction was complete at 160.degree. pot temp. Excess solvent and fumarate were distd. under high vacuum to give product, sapon equiv. 186. Also, 322 g. di-Et fumarate and 284 g. I similarly reacted in benzene with 4 ml. tetra-Bu titanate after water removal. The products were polymerized with an equal wt. of styrene. The heat distortion points of the samples were 133.degree. and 124.degree., resp.

CC 10E (Organic Chemistry: Benzene Derivatives)

L25 ANSWER 31 OF 31 HCA COPYRIGHT 2002 ACS

40:20700 Original Reference No. 40:4036c-e Relative efficiency of some polymerization inhibitors. Frank, Robert L.; Adams, Clark E. (Univ.

of Illinois, Urbana). J. Am. Chem. Soc., 68, 908 (Unavailable) 1946.

- AB Tests are reported for **styrene**, 3,4-**dichlorostyrene**, and 5-ethyl-2-vinylpyridine in which the inhibition period (heating time required to show a difference in flow time) and the total time of polymerization (samples too viscous to give a measurable flow time) were detd. for the following inhibitors: picric acid (I), C₆H₃(NO₃)₃ (II), 2,5,1,4-(HO)₂C₆H₂O₂, 1,4-C₁₀H₆O₂, 1,4-C₆H₄O₂, chloranil, 9,10-phenanthrenequinone, tert-**butylcatechol** (III), 4,1-H₂NC₁₀H₆OH, 1,4-C₆H₄(OH)₂, 2-C₁₀H₇NHPh (IV), and Ph₃PO₃. There appears to be no great variation in the order of inhibitory strength from 1 **monomer** to another; a good inhibitor for 1 **monomer** is likely to be good for another, III and IV, 2 widely used inhibitors, are among the poorest in inhibitory action, at least for the **monomers** tried. I and II are being used with great success during **distn.** of a wide variety of **monomers**. The use of traces should involve no danger of explosion. I should not be used in metal containers.
- CC 10 (Organic Chemistry)

=> d 127 1-8 cbib abs hitind

- L27 ANSWER 1 OF 8 HCA COPYRIGHT 2002 ACS
136:217179 Method for **distillation** of **alkoxystyrene** compounds. Oda, Yasuhiro; Eguchi, Hisao (Tosoh Corp., Japan). Jpn. Kokai Tokkyo Koho JP 2002069025 A2 20020308, 5 pp. (Japanese).
CODEN: JKXXAF. APPLICATION: JP 2000-259391 20000824.

GI

HC CH₂

OR

I

- AB The title method comprises **distg.** the title compds. I [R = alkyl, etc.] in the presence of an epoxy compd. and a nitroso compd. and/or a nitro compd. **Alkoxystyrenes** are raw materials for polymers and intermediates for pharmaceuticals and agrochems. Thus, **distn.** of tert-**butoxystyrene** (II) in the presence of 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexylcarboxylate and N-nitrosophenylhydroxylamine aluminum salt gave II with 99.9% purity, vs. 96.5% purity in a ref. process.
- IC ICM C07C041-46
ICS C07C041-42; C07C043-215; C07C069-157
- CC 35-2 (Chemistry of Synthetic High Polymers)

- Section cross-reference(s): 1, 5
- ST **alkoxystyrene distn, butoxystyrene distn**
- IT **Distillation**
(method for **distn.** of **alkoxystyrene**)
- IT Epoxy resins, uses
(method for **distn.** of **alkoxystyrene** in presence of bisphenol A type epoxy resins)
- IT Epoxides
(method for **distn.** of **alkoxystyrene** in presence of epoxides)
- IT 51-28-5, 2,4-Dinitrophenol, uses 98-29-3, p-tert-**Butylcatechol** 99-65-0, m-Dinitrobenzene 135-20-6 148-97-0 2386-87-0, 3,4-Epoxy cyclohexylmethyl 3',4'-epoxycyclohexylcarboxylate 15305-07-4 25550-58-7, Dinitrophenol
(method for **distn.** of **alkoxystyrene**)
- IT 2628-16-2P, p-**Acetoxystyrene** 59858-52-5P, **Acetoxystyrene** 95418-58-9P, p-tert-**Butoxystyrene** 105612-79-1P 153723-74-1P, tert-**Butoxystyrene**
(method for **distn.** of **alkoxystyrene**)
- L27 ANSWER 2 OF 8 HCA COPYRIGHT 2002 ACS
- 136:135155 Procedure for the **distillation** of **vinylaromatic monomers** in the presence of oxygen and 4-tertiary-**butylcatechol** as polymerization inhibitors. Schmaus, Paulus; Metzger, Werner Georg (BASF A.-G., Germany). Ger. DE 10038349 C1 20020131, 4 pp. (German). CODEN: GWXXAW. APPLICATION: DE 2000-10038349 20000805.
- AB A procedure for the **distn.** of **vinylarom. monomers** in the presence of 4-tert-**butylcatechol** and oxygen, where no arom. nitro or amine compd. is present in effective quantities, is presented. The procedure is suitable for the stabilization and cleaning of **styrene** stabilized for transportation with 4-tert-**butylcatechol**.
- IC ICM C07C007-04
ICS C07C007-20; C07C015-44; C07C015-46
- CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 25, 48
- ST **vinylarom monomer distn** oxygen
butylcatechol, purifn **vinylarom monomer distn** oxygen **butylcatechol**, **styrene distn** oxygen **butylcatechol**
- IT **Distillation**
Polymerization inhibitors
(procedure for the **distn.** of **vinylarom. monomers** in the presence of oxygen and 4-tertiary-**butylcatechol** as polymn. inhibitors)
- IT **Distillation** apparatus
(procedure for the **distn.** of **vinylarom. monomers** in the presence of oxygen and 4-tertiary-**butylcatechol** as polymn. inhibitors in a)
- IT **Aromatic compounds**

Vinyl compounds, uses

(vinyl arenes; procedure for the **distn.** of vinylarom. monomers in the presence of oxygen and 4-tertiary-butylcatechol as polymn. inhibitors in a)

IT Monomers

(vinylarom. compds.; procedure for the **distn.** of vinylarom. monomers in the presence of oxygen and 4-tertiary-butylcatechol as polymn. inhibitors in a)

IT 98-29-3, 4-tert-Butylcatechol 7782-44-7,

Oxygen, uses

(polymn. inhibitors in the **distn.** of vinylarom. monomers in the presence of)

IT 9003-53-6P, Polystyrene

(procedure for the **distn.** of vinylarom. monomers in the presence of oxygen and 4-tertiary-butylcatechol as polymn. inhibitors)

IT 100-42-5P, Styrene, preparation

(procedure for the **distn.** of vinylarom. monomers in the presence of oxygen and 4-tertiary-butylcatechol as polymn. inhibitors)

L27 ANSWER 3 OF 8 HCA COPYRIGHT 2002 ACS

134:4760 Method for **distillation** of **hydroxystyrene**

ethers and esters. Ishikawa, Shinichi; Soga, Shinichi; Eguchi, Hisao (Tosoh Corp., Japan). Jpn. Kokai Tokkyo Koho JP 2000327617 A2 20001128, 6 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1999-327155 19991117. PRIORITY: JP 1998-341559 19981201; JP 1999-73510 19990318.

GI

CH₂

OR

I

AB The title compds. (I; R = alkyl, aryl, arylalkyl, alkoxyalkyl, alkylcarbonyl, alkoxy carbonyl, alkylsilyl) are economically **distd.** in high recovery ratio with very little formation of polymers using nitroso compd. and/or nitro compd. as polymn. inhibitors. Thus, 10 g p-tert-butoxystyrene (PTBS) and 0.01 g N-nitrosophenylhydroxylamine ammonium salt were added to a flask fitted with a reflux condenser and refluxed at 120.degree. and 5 mmHg for 16 h while **air** being passed into the liq. through a capillary tube. A sample of PTBS was analyzed by liq.

chromatog. (GPC-2000 column) to show the formation of polymer by 0.4%.

- IC ICM C07C041-42
ICS C07B063-04; C07C041-46; C07C043-215; C07C067-54; C07C067-62; C07C069-157
- CC 25-18 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)
- ST **distn hydroxystyrene** ether ester; nitroso nitro compd polymn inhibitor
- IT **Distillation**
Polymerization inhibitors
(**distn.** of **hydroxystyrene** ethers and esters using nitroso compd. and/or nitro compd. as polymn. inhibitors.)
- IT Nitro compounds
Nitroso compounds
(**distn.** of **hydroxystyrene** ethers and esters using nitroso compd. and/or nitro compd. as polymn. inhibitors.)
- IT 51-28-5, 2,4-Dinitrophenol, uses **98-29-3**, p-tert-**Butylcatechol** 99-65-0, m-Dinitrobenzene 104-91-6, p-Nitrosophenol 135-20-6
(**distn.** of **hydroxystyrene** ethers and esters using nitroso compd. and/or nitro compd. as polymn. inhibitors.)
- IT 2628-16-2P, p-**Acetoxystyrene** 95418-58-9P, p-tert-**Butoxystyrene** 105612-79-1P, m-tert-**Butoxystyrene**
(**distn.** of **hydroxystyrene** ethers and esters using nitroso compd. and/or nitro compd. as polymn. inhibitors.)

L27 ANSWER 4 OF 8 HCA COPYRIGHT 2002 ACS

- 101:152851 Polymerization co-inhibitors for **vinyl aromatic** compounds. Butler, James R.; Watson, James M.; Kendall, Debra L.; Mikkelsen, Karen A. (Cosden Technology, Inc., USA). U.S. US 4468343 A 19840828, 9 pp. (English). CODEN: USXXAM. APPLICATION: US 1983-483976 19830411.
- AB **Arom. vinyl monomers** are inhibited against polymn. during heating by a compn. contg. 2,6-dinitro-p-cresol (I) [609-93-8] and a phenylenediamine deriv. or 4-tert-**butylcatechol** [98-29-3]. Thus, 25 g **styrene** [100-42-5] contg. 100 ppm I and 50 ppm Flexone 4L [N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine] [3081-14-9] was heated 2 h at 138 +/- 2.degree. to give **monomer** contg. 14.94% polymer, compared to 18.24% for **styrene** contg. I only.
- IC C09K015-22; C08F002-38
- NCL 252403000
- CC 37-2 (Plastics Manufacture and Processing)
- ST **styrene** polymn inhibitor; nitrocresol polymn inhibitor **styrene**; phenylenediamine polymn inhibitor **styrene**; **butylcatechol** polymn inhibitor **styrene**
- IT Polymerization inhibitors
(dinitrocresol-phenylenediamine deriv. compns., for **arom vinyl monomers**)
- IT 100-42-5, uses and miscellaneous
(polymn. inhibitors for, dinitrocresol-phenylenediamine deriv.

- compns. as)
IT 100-42-5D, derivs. 1321-74-0, uses and miscellaneous
25013-15-4 26588-32-9
(polymn. inhibitors for, dinitrocresol-phenylenediamine deriv.
compns. as)
IT 98-29-3 609-93-8 3081-14-9
(polymn. inhibitors, for **styrene**)
IT 100-41-4P, uses and miscellaneous
(**styrene** mixts., **distn.** of, polymn.
inhibitors for)

L27 ANSWER 5 OF 8 HCA COPYRIGHT 2002 ACS

101:152850 Polymerization inhibition process for **vinyl**

aromatic compounds. Butler, James R.; Watson, James M.;
Kendall, Debra L.; Mikkelsen, Karen A. (Cosden Technology, Inc.,
USA). U.S. US 4466905 A 19840821, 9 pp. (English). CODEN:
USXXAM. APPLICATION: US 1983-483978 19830411.

- AB **Arom. vinyl monomers** are inhibited
against polymn. during **distn.** by a compn. contg.
2,6-dinitro-p-cresol (I) [609-93-8] and a phenylenediamine deriv.
or 4-tert-**butylcatechol** [98-29-3]. Thus, 25 g
styrene [100-42-5] contg. 100 ppm I and 50 ppm
Flexone 4L [N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine]
[3081-14-9] was heated 2 h at 138 .+-. 2.degree. to give
monomer contg. 14.94% polymer, compared to 18.24% for
styrene contg. I only.

IC C09K015-22; C08F002-38

NCL 252403000

CC 37-2 (Plastics Manufacture and Processing)

ST **styrene** polymn inhibitor; nitrocresol polymn inhibitor
styrene; phenylenediamine polymn inhibitor **styrene**
; **butylcatechol** polymn inhibitor **styrene**

IT Polymerization inhibitors
(dinitrocresol-phenylenediamine deriv. compns., for **arom**
vinyl monomers)

IT 100-42-5, uses and miscellaneous 100-42-5D,
derivs. 1321-74-0, uses and miscellaneous 25013-15-4
26588-32-9
(polymn. inhibitors for, dinitrocresol-phenylenediamine deriv.
compns. as)

IT 98-29-3 609-93-8 3081-14-9
(polymn. inhibitors, for **styrene**)

IT 100-41-4P, uses and miscellaneous
(**styrene** mixts., **distn.** of, polymn.
inhibitors for)

L27 ANSWER 6 OF 8 HCA COPYRIGHT 2002 ACS

94:65294 **Distillation** of light polymerizable **aromatic**

vinyl compounds. Watson, James M. (Cosden Technology, Inc.,
USA). Ger. Offen. DE 2914226 19801023, 35 pp. Addn. to Ger. Offen.
2,804,449. (German). CODEN: GWXXBX. APPLICATION: DE 1979-2914226
19790409.

- AB The title compds. were **distd.** using 4,2,6-Me(O₂N)₂C₆H₂OH as polymn. inhibitor. Thus, **styrene**, free of tert-butylcatechol, was refluxed in the presence of air and 4,2,6-Me(O₂N)₂C₆H₂OH. No polymeric **styrene** was formed even after 5 h.
- IC C07C015-44; C07C007-20
- CC 25-2 (Noncondensed Aromatic Compounds)
- ST **styrene** polymn inhibitor; dinitrocresol **arom vinyl** polymn inhibitor
- IT Polymerization inhibitors
(2,6-dinitro-p-cresol, for **arom. vinyl** compds.)
- IT **Vinyl** compounds, reactions
(**arom.**, polymn. of, inhibition of, by 2,6-dinitro-p-cresol)
- IT 609-93-8
(polymn. inhibitor for **styrene** and **arom. vinyl** compds.)
- IT 100-42-5, reactions
(polymn. of, inhibition of, by 2,6-dinitro-p-cresol)
- L27 ANSWER 7 OF 8 HCA COPYRIGHT 2002 ACS
- 78:136989 Separation of **styrene**. Iida, Hiroshi; Tatsumi, Masanori (Toray Industries, Inc.). Jpn. Kokai Tokkyo Koho JP 48010031 19730208 Showa, 4 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1971-44862 19710623.
- AB **Styrene** (I) [100-42-5] was sepd. from C8 **arom.** hydrocarbon fractions by extractive **distn.** with an org. polar solvent in the presence of 50-2000 ppm of an alkali metal nitrite and 50-2000 ppm of an **arom.** compd. contg. quinoid, OH, NO, or NO₂ groups, e.g. p-tert-butylpyrocatechol (II) [98-29-3], o-nitrophenol [88-75-5], p-dinitrobenzene [100-25-4], p-benzoquinone [106-51-4], or .alpha.-naphthoquinone [130-15-4]. Thus, a C8 **arom.** hydrocarbon fraction (90 ml/hr) was fed into the 50th plate (from the bottom) of an Oldershaw type column and AcNMe₂ contg. 3000 ppm sodium nitrite [7632-00-0] and 200 ppm II into the 5th plate (from the top) at 120 ml/hr, and extn. was carried out at 130.deg. (at the bottom), 150 mm (at the top), and with a reflux ratio of 8 to give I of 99% purity. Loss of I by thermal polymn. was <0.1% compared with 0.5% without II addn.
- NCL 16CL
- CC 35-2 (Synthetic High Polymers)
Section cross-reference(s): 25
- ST **styrene** sepn **arom** hydrocarbon; pyrocatechol **styrene** purifn; nitrophenol **styrene** purifn; benzoquinone **styrene** purifn; naphthoquinone **styrene** purifn; **distn** extractive **styrene**; nitrite **styrene** purifn
- IT Polymerization inhibitors
(nitro compds., phenols, quinones and nitrites, for **styrene**)
- IT Nitrites

- (polymn. inhibitors, for **styrene**)
- IT 100-42-5P, preparation
(manuf. of, polymn. inhibitors for use in)
- IT 88-75-5 98-29-3 100-25-4 106-51-4, uses and
miscellaneous 130-15-4 7632-00-0
(polymn. inhibitors, for **styrene**)
- L27 ANSWER 8 OF 8 HCA COPYRIGHT 2002 ACS
- 70:11236 Inhibitors of vinyltoluene polymerization. Lazareva, E. V.;
Telegin, V. G.; Sidorov, V. A.; Bezrukova, A. P. (USSR). Khim.
Prom. (Moscow), 44(9), 660-2 (Russian) 1968. CODEN: KPRMAW.
- AB During **distn.** at 100.degree. unstabilized vinyltoluene (I)
undergoes polymn. (15% and 20% during 3 hrs. when **distd.**
under N or in the presence of **air**, resp.). Samples of I
(purity 99.7-9.9%) contg. 0.010-0.100% inhibitors were heated at
100.degree. or 110.degree. under slight N pressure or in **air**
for 3, 6, or 12 hrs. and the decrease in I contents were detd. by
potentiometric titrn. The following inhibitors were tested: S,
hydroquinone (II) Metol [(p-MeHNC6H4OH)2H2SO4], Nonox(2,4-dimethyl-6-
octylphenol), p-PhCH2HNC6H4OH, o-O2NC6H4OH (III), Ionol
(2,6-di-tertbutyl-4-methylphenol), Antioxidant 2246
[2,2'-methylenebis-(4-methyl-6-tert-butylphenol)], (p-HOC6H4)2NH,
Neozone A (phenyl-.alpha.-naphthylamine), .alpha.-naphthylamine,
.beta.-naphthylamine, p-bis(di-.beta.-naphthylamino)benzene,
p-Ph2NC6H4NPh2, p-(N-phenylamino)-N-cyclohexylaniline, a C17-20
amine fraction, dicyclohexylamine, 2,4-dinitrotoluene (IV),
bis(2,4-dinitrophenyl)-amine (V), NaNO3, 1,3-dinitrobenzene,
4-nitro-2-aminophenol, p-quinone dioxime (VI), chloranil,
anthraquinone, 8-hydroxyquinoline, bisphenol A, dicresylolpropane,
.alpha.-naphthol, 4-tert-butylpyrocatechol (VII),
4-tert-octylpyrocatechol. Satisfactory stabilization was obtained
with S, III, IV, V, VI, and VII. One of the best was a mixt. of
0.1% III with 0.05% II.
- CC 25 (Noncondensed Aromatic Compounds)
- IT Polymerization inhibitors
(for **methylstyrene**)
- IT 7704-34-9, uses and miscellaneous
(as inhibitor for polymn. of **methylstyrene**)
- IT 25013-15-4
(polymn. inhibitors for)
- IT 88-75-5 98-29-3 105-11-3 118-75-2, uses and
miscellaneous 121-14-2 961-68-2 7704-34-9, uses and
miscellaneous
(polymn. inhibitors, for **methylstyrene**)

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- L28 ANSWER 1 OF 3 HCA COPYRIGHT 2002 ACS
- 89:90437 Polymerization inhibitor for **vinyl aromatic**
compounds. Watson, James M. (Cosden Technology, Inc., USA). U.S.
US 4086147 19780425, 4 pp. (English). CODEN: USXXAM. APPLICATION:

US 1976-749406 19761210.

- AB Readily-polymerizable **vinyl arom. monomers** are purified by **distn.** in the presence of m-nitro-p-cresol (I) [2042-14-0] polymn. inhibitor. Thus, 200 ppm I was added to 50 g **styrene** [100-42-5] free of tert-butylcatechol and the whole was kept at 115 +/- 2.degree. for 4 h without significant pptn. of polymer (4.2%), compared to 7.5% for 2,4-dinitrophenol, a known inhibitor. I was only slightly less effective than the toxic polymn. inhibitor 4,6-dinitro-c-cresol.
- IC B01D003-34
- NCL 203009000
- CC 35-2 (Synthetic High Polymers)
- ST nitrocresol polymn inhibitor **styrene**; safety inhibitor **distn styrene**
- IT Polymerization inhibitors
(nitrocresol, for **styrene**)
- IT Safety
(nontoxic polymn. inhibitors, for **styrene**, nitrocresol as)
- IT 2042-14-0
(polymn. inhibitors, for **styrene**)
- IT 100-42-5P, preparation
(purifn. by **distn.** of, polymn. inhibitors for, nitrocresol as)

L28 ANSWER 2 OF 3 HCA COPYRIGHT 2002 ACS

52:61246 Original Reference No. 52:11082g-i,11083a-e Preparation of polymers and copolymers from vinylpyrimidines and triazines. Overberger, C. G.; Michelotti, Francis W. (Polytech. Inst. of Brooklyn, Brooklyn, NY). J. Am. Chem. Soc., 80, 988-91 (Unavailable) 1958.

- AB Com. **styrene** washed with 5% aq. NaOH and H₂O, dried, and **distd.** yielded pure **styrene**, b₂₀ 47-8.degree., n_{25D} 1.5442. Com. CH₂:CHAc dried with Na₂SO₄, treated with p-tert-butylcatechol, and **distd.** gave pure material, b. 81.4.degree. n_{25D} 1.4086. [H₂NC(:NH)]₂NH (I) sulfate (30 g.) in 250 cc. H₂O treated simultaneously with 20.5 g. AcCl and 21.5 g. NaOH in 100 cc. H₂O during 0.5 hr. with cooling and stirring, stirred 0.5 hr., and filtered yielded 4.95 g. 4,6-diamino-2-vinyl-s-triazine (II), decomp. 300-10.degree. without melting (H₂O). II (1 g.) in 200 cc. H₂O and 1 cc. concd. HCl hydrogenated over 0.5 g. PtO₂, filtered, treated with stirring slowly with 0.48 g. NaOH in 10 cc. H₂O, and filtered yielded 0.4 g. 2-Et analog (III) of II, m. 308.degree. (H₂O). I (2 g.) in 50 cc. abs. MeOH heated gently 1 hr. with 2.1 g. EtCO₂Et, cooled, and filtered gave 0.7 g. III. II (0.85 g.) dissolved under N in 75 cc. H₂O, treated with 0.002 g. K peroxydisulfuric acid (IV), heated 5 min., and filtered, and the residue washed with abs. EtOH and dried in vacuo yielded 0.75 g. polymeric II, powder; it showed an intrinsic viscosity of 2.05 in 0.1N HCl and KCl. 4-Vinylpyrimidine (V) (0.50 g.) in 5 cc. dry PhMe treated with 0.0035 g. [Me₂C(CN)N:]₂ (VI), degassed, heated 9 hrs.

in a sealed tube at 59.9.degree., and filtered, the residue washed with a few cc. PhMe and dried in vacuo, the crude solid (0.368 g.) dissolved in MeOH-HCONMe₂ and repptd. with dry Et₂O, the repptn. repeated, the final ppt. dissolved in 10 cc. H₂O, and the soln. filtered and freeze-dried gave 0.35 g. polymeric V, fluffy white solid which held traces of H₂O tenaciously. 2-(Dimethylamino)-4-vinylpyrimidine (VII) (0.51 g.) in 5 cc. dry PhMe treated with 2 mg. VI, degassed in vacuo, heated 9 hrs. at 59.9.degree. in a sealed tube, and treated dropwise with stirring with 30 cc. dry Et₂O, and the gummy ppt. washed with Et₂O, dissolved in 15 cc. C₆H₆, and repptd. with dry Et₂O gave in the usual manner polymeric VII; intrinsic viscosity in C₆H₆ 1.8. V (0.494 g.) and 0.663 g. VII in 5 cc. dry PhMe treated with 0.0075 g. VI, polymerized in the usual manner at 59.9.degree., and processed gave 0.85 g. V-VII copolymer. Similarly were copolymerized in HCONMe₂ V with II and VII with II. A series of copolymerization runs in dry PhMe was carried out in the usual manner in the presence of 0.5 mole-% VI and the reaction stopped below 10% conversion by cooling to -78.degree.; thus **styrene** and VII gave the following results (mole-% VII in **monomer** mixt., reaction time in min., % conversion, and mole fraction VII in polymer given): 10, 60, 0.4, 0.216; 25, 60, 3.0, 0.423; 50, 80, 9.4, 0.642; 65, 38, 6.1, 0.756; 75, 18, 2.0, 0.823; 85, 12, 1.3, 0.891. **Styrene** and V gave the following results (mole-% V in **monomer** mixt., reaction time in min., % conversion, and mole fraction V in polymer given): 10, 58, 3.0, 0.302; 25, 32, 3.2, 0.488; 50, 15, 0.51, 0.755; 65, 27, 5.3, 0.820; 75, 20, 4.3, -. A similar series of copolymerization runs was performed with CH₂:CHAc and II in the presence of 0.5 mole % IV (mole-% CH₂:CHAc in **monomer** mixt., reaction time in min., % conversion, and mole fraction CH₂:CHAc in polymer given): 10, 5.5, 2.2, 0.300; 34, 3.3, 0.2, 0.550; 53, 3.5, 4.3, 0.712; 75, 3.0, 3.0, 0.813; 90, 5.3, 6.6, 0.824. The **monomer** reactivity ratios were calcd. from these data.

CC 10 (Organic Chemistry)

L28 ANSWER 3 OF 3 HCA COPYRIGHT 2002 ACS

49:36035 Original Reference No. 49:6964f-i,6965a-i,6966a-d

Monomer synthesis. X. The preparation and polymerization of 4-vinylpyrimidine and 2-dimethylamino-4-vinylpyrimidine.

Overberger, C. G.; Kogon, Irving C. (Polytech. Inst. of Brooklyn, Brooklyn, NY). J. Am. Chem. Soc., 76, 1879-83 (Unavailable) 1954.

AB cf. C.A. 49, 3982a. Convenient syntheses of 4-vinylpyrimidine (I) and 2-dimethylamino-4-vinylpyrimidine (II) are described. The general reaction consists of the conversion of the appropriate methylpyrimidine to the (2-hydroxyethyl) deriv., then dehydration over solid KOH. A no. of derivs. of I and II are described. Polymers have been prep'd. by radical catalysis and characterized. The vinylpyrimidines are inactive against sarcoma 180. [Me₂NC(:NH₂)NH₂]₂SO₄ (54.4 g.) added to NaOMe from 10.1 g. Na and 240 cc. MeOH, the mixt. refluxed 0.5 hr., cooled, treated with 63.2 g. tech. AcCH₂CO₂Et, refluxed 23 hrs., cooled, dild. with 200 cc. H₂O, carefully neutralized with AcOH, extd. continuously 24 hrs.

with CH_2Cl_2 , the ext. dried with Na_2SO_4 , evapd., and the residue recrystd. from iso-PrOH gave 47 g. (77%) 2-dimethylamino-4-hydroxy-6-methylpyrimidine (III), white crystals, m. 175-6.degree. (all m.ps. are cor.), yielding in Et₂O a picrate, m. 206-8.degree., which recrystd. from EtOH in yellow needles, m. 207-8.degree.. II (30.6 g.) and 80 cc. POCl_3 refluxed 4 hrs., the amber soln. poured into approx. 400 g. ice and H_2O , treated 10 min. with Norit, filtered, cooled to 0-5.degree., carefully neutralized with 27% NH_4OH , and the resulting white cryst. ppt. sublimed at 30.degree./0.1 mm. gave 34.2 g. (90.5%) 4-chloro-2-dimethylamino-6-methylpyrimidine (IV), m. 35-6.degree.; picrate, m. 128-9.degree. (from EtOH). IV (2.5 g.), 6.0 g. MgO , 45 cc. EtOH, 90 cc. H_2O , and 0.1 g. 10% Pd-C hydrogenated 45 min. at room temp., the mixt. filtered, washed with EtOH, extd. continuously 20 hrs. with CH_2Cl_2 , the ext. dried 24 hrs. with Na_2SO_4 , evapd., and the residue **distd.** gave 5.6 g. (82.4%) 2-dimethylamino-4-methylpyrimidine (V), b₂₀ 85-8.degree.; redistn. yielded 5.4 g. (79.5%) pure V, colorless liquid, b₄₀ 103-6.degree., n_D25 1.5323, d₂₅ 1.0195. V (69.5 g.) (sealed into 3 tubes) and 11.25 g. paraformaldehyde heated 24 hrs. at 162.degree. the mixt. rinsed from the tubes with CHCl_3 , the soln. dried with Na_2SO_4 , evapd., and the residue **distd.** gave 30 g. (43%) V, b₁₅ 84-5.degree. n_D25 1.5328 (picrate, m. 146-8.degree.); 7.0 g. slightly yellow, limpid liquid, b_{6.0} 93-5.degree.; 4.0 g. slightly viscous liquid, b_{0.4} 123-33.degree.; 4.0 g. viscous liquid, b_{0.5} 165-70.degree., which solidified on standing; and approx. 25 g. tarry, nondistillable residue. The 2nd fraction redistd. gave 4 g. V and 2.0 g. II, slightly yellow colored liquid, b₁₀ 95-8.degree., n_D25 1.5604, d₂₅ 1.0853, turning yellow on standing at room temp. but remaining almost colorless when refrigerated several months. II in Et₂O with excess picric acid in Et₂O gave the picrate, m. 128.5-31.5.degree. (from EtOH). The 3rd-fraction redistd. gave 3.0 g. 2-dimethylamino-4-(2-hydroxyethyl)pyrimidine (VI), light yellow liquid, b_{1.5} 123-5.degree., n_D25 1.5539, d₂₅ 1.1150; the solidified **distillate** recrystd. twice from iso-PrOH yielded 2.0 g. white cryst. solid, C₁₅H₂₂N₆, m. 109-10.degree., which, on the basis of its analysis and mol. wt., had a dimeric structure. Into each of 4 vinyl polymerization tubes were sealed 13.7 g. V and 25 g. paraformaldehyde, the tubes heated 3.5 hrs. at 150.degree., the mixts. rinsed out with CHCl_3 , the CHCl_3 solns. dried with Na_2SO_4 , evapd., and the residues **distd.**, giving 35 g. (64%) recovered V, b₁₅ 84-6.degree., n_D25 1.5321; 4.0 g. light yellow liquid, b₁₅ 98-105.degree.; and 10 g. yellow, viscous liquid, b₄ 130-40.degree.. The 2nd fraction redistd. gave 2.2 g. II, colorless liquid, b₁₅ 103-5.degree. n_D25 1.5605; the 3rd fraction redistd. gave 8 g. VI, n_D25 1.5536. VI (6 g.) added dropwise during 2 min. to 80 g. KOH pellets at 160.degree. and 10 mm. pressure, the resulting **distillate** extd. 3 times with 15-cc. portions of Et₂O, the ext. dried with Na_2SO_4 , evapd., and the residue **distd.** gave 2.5 g. (46.7%) II, light yellow liquid, b₁₄ 95-8.degree., n_D25 1.5608 (picrate, m. 130-3.degree.). II (1.49 g.) in 20 cc. EtOH hydrogenated 1 hr. at 1.5 atm. over 0.1 g. 10% Pd-C, the catalyst filtered, washed with EtOH, the combined filtrate and

washing evapd., and the residue **distd.** gave 0.75 g. (50%) 2-dimethylamino-4-ethylpyrimidine, b15 91-2.degree., nD25 1.5274, d25 1.0037; picrate, m. 109-11.degree. (recrystd. from EtOH, m. 110-11.degree.). V (13.7 g.), 8.0 g. 37% CH2O, 7.8 g. Me2NH.HCl, and 10 cc. abs. EtOH refluxed 1 hr., the yellow soln. cooled, made basic to litmus with 30% NaOH, extd. with 25 cc. CHCl3, dried 20 hrs. with K2CO3, evapd., and the residue **distd.** gave 6.8 g. (50%) recovered V, and 7.0 g. (72.2%) 2-dimethylamino-4-(2-dimethylaminoethyl)pyrimidine, b5 134-5.degree. yellow liquid, which redistd. gave 6.4 g. (66%) pure product, pale yellow liquid, b6 135-6.degree., nD25 1.5368, d25 1.0299; picrate, m. 152.2-3.2.degree. (from EtOH). II (1 g.), 0.05 g. (:NCMe2CN)2 (VII), and 10 cc. dry PhMe heated 5 hrs. in a sealed tube (previously evacuated 5 times at 10-5 mm.), the solvent removed, the residue dissolved in MeOH, the soln. dild. with H2O, and the tan cryst. ppt. filtered off and dried 24 hrs. over concd. H2SO4 in a vacuum desiccator gave 0.4 g. polymeric II, m. 95.degree. (decompn.) with softening at 85.degree.; its analysis and mol. wt. indicated that catalyst fragments were incorporated in the polymer. II (0.5 g.), 0.5 g. **styrene**, and 25 mg. VII heated 6 hrs. in a vinyl polymerization tube, the resulting yellow viscous mixt. dissolved in 2 cc. EtAc, the soln. added dropwise to 200 cc. MeOH, and the ppt. repptd. twice from EtAc with MeOH gave a II-**styrene** copolymer. 2,4-Dichloro-6-methylpyrimidine (20.4 g.), 18 g. MgO, 90 cc. abs. EtOH, and 180 cc. H2O hydrogenated 1 hr. over 1.2 g. 10% Pd-C at room temp. and 1-2 atm. pressure, the mixt. filtered, the filtrate washed with H2O and CH2Cl2, extd. 48 hrs. continuously with CH2Cl2, the ext. dried 48 hrs. with K2CO3, evapd., and the residue fractionated gave 3.5 g. (30%) 4-methylpyrimidine (VIII), b760 141-5.degree., nD25 1.4940, and 6 g. tarry residue. VIII in Et2O with excess picric acid in Et2O gave the picrate, yellow crystals, m. 132-2.2.degree., and with aq. HgCl2 the mercurichloride deriv., m. 198-9.degree.. When MeOH was used instead of EtOH in a similar run 2,4-dimethoxy-6-methylpyrimidine, white crystals, m. 69-70.degree., was obtained. A similar run with 27% NH4OH and MeOH gave 30% VIII, and run with NH3 in MeOH yielded 28.3% VIII. VIII (10 g.) and 3.0 g. paraformaldehyde heated 3.5 hrs. in a sealed tube at 165.degree., the mixt. rinsed out with Et2O, the solvent removed, and the residue **distd.** gave 6 g. (60%) VIII, b760 140-1.degree., and 4.0 g. (87%) crude 4-(2-hydroxyethyl)-pyrimidine (IX), b10 132-9.degree., which redistd. yielded 3.5 g. (76%) pure IX, viscous liquid with a yellow tinge and a rancid odor, b9 125-7.degree., nD25 1.5323, d25 1.3620. IX (10 g.) and 0.1 g. p-tert-**butylcatechol** added dropwise during 3 min. in the usual manner to KOH pellets, the resulting **distd.** mixt. collected in a Dry Ice trap, extd. 3 times with 45-cc. portions of Et2O, the ext. dried 24 hrs. with Na2SO4, evapd., and the residue **distd.** gave 2 g. (23.4 g.) I, colorless liquid, b10 56-8.degree., nD25 1.5405, d25 1.0598, turning red on standing; picrate, m. 125-30.degree., could not be recrystd. I (1.2 g.), 50 mg. 10% Pd-C, and 35 cc. abs. EtOH hydrogenated 1 hr., the mixt. filtered, the filter cake washed with EtOH, the combined

filtrate and washing evapd., and the residue fractionated gave 0.8 g. (66%) 4-ethylpyrimidine, b10 65-7.degree., nD25 1.4817, d25 0.9981; picrate, m. 85-6.degree. (recrystd. from EtOH, m. 85.5-86.degree.). VIII (4.7 g.), 9 g. 25% aq. Me2NH, 4.5 cc. concd. HCl, and 4.0 g. 37% aq. CH2O refluxed 1 hr., the yellow soln. cooled, neutralized with 20% aq. NaOH, extd. with 20 cc. CHCl3, the ext. dried with K2CO3, evapd., and the residue **distd.** gave 2 g. recovered VII and 3 g. (70%) 4-(2-dimethylaminoethyl)pyrimidine, b30 120-22.degree., nD25 1.5145, d25 1.0205. I (0.7 g.), 0.0375 g.VII, and 7.5 cc. dry PhMe sealed in a tube evacuated to 10-5 mm. heated 4 hrs. on the steam bath, the solvent decanted, the heavy, viscous oily residue washed with 1 cc. PhMe, dissolved in 3 cc. MeOH, and the soln. treated with Norit and then dild. with Et2O pptd. 0.3 g. polymeric I, tan amorphous solid, m. 127-42.degree. (decompn.), mol. wt. 873; the analysis indicated that catalyst fragments were present in the polymer.

CC 10 (Organic Chemistry)

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FILE 'HCA' ENTERED AT 10:16:08 ON 18 SEP 2002

L29	QUE ?NITRO? OR ?AMINO? OR NO2 OR NH2
L30	61 S L10 NOT L29
L31	25 S L30 NOT (L26 OR L27 OR L25 OR L28)
L32	0 S L31 AND L5 AND L19
L33	0 S L31 AND (L12 OR L17)